Second Edition

A Textbook of Statistical Mechanics

Suresh Chandra | Mohit Kumar Sharma

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Statistical Mechanics

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Statistical Mechanics

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to

---

my hon'ble mother
Mrs Ramkatori Sharma
and hon'ble father
Shri Chiranji Lal Sharma
who left for heavenly abode on
19 November 2002 and 18 April 2003

— Suresh Chandra

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Preface to the Second Edition

The response to the first edition of the book was very encouraging. We received appreciation and constructive suggestions from our friends, teachers and students. It is learnt that some universities are using this book as a textbook for the paper 'Statistical Mechanics' for MSc physics and chemistry students. The content of the first edition of the book has been revised thoroughly. Further, one chapter on 'Thermodynamics' is included. I hope, the second edition would prove to be more useful to the students.

There is always scope for further improvement. We shall appreciate receiving comments/suggestions, which can be sent at the following e-mails *suresh492000@yahoo.co.in* and *mohitkumarsharma32@yahoo.in*

It is our pleasure to thank a number of colleagues in India and abroad who are consulting this book for their classroom teaching and research work, and have sent their valuable comments/suggestions so that a new version of the book is brought out. We received feedback from the students in various universities in India as well as abroad. We are thankful to all of them.

Suresh Chandra
Mohit Kumar Sharma

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Preface to the First Edition

Statistical mechanics is one of the fundamental papers for MSc physics and chemistry courses. This book can be used as a textbook for these courses. Basically, the text presented here is the print form of my classnotes which have been revised from time to time. One of the policies followed in this book has been to discuss each topic in detail and in a systematic manner by developing it from the level of the existing knowledge of a common student to the required level of the MSc study in an easily understandable mode as well as language. Topics are supplemented by examples which further help in better understanding of the subject.

While preparing the manuscript, I consulted various books and got their help. I am grateful to the authors and publishers of those books. Besides the books listed here, information about other books on the topic is available on the website: http://stp.clarku.edu/books. For this book, I have been helped, advised, and encouraged by my friends working in various institutions/universities in India as well as abroad, and by my friends in personal life. I am heartily thankful to all of them. I would like to thank my students whom I taught the subject and got feedback for improvement of the notes. I would greatly appreciate receiving comments and suggestions from the students, my friend teachers and others. These can be sent at my e-mail address: suresh492000@yahoo.co.in or through ordinary mail.

I am grateful to Prof JV Narlikar, Prof Dr WH Kegel and Prof SP Khare for their encouragement. I am thankful to Dr Pramod G Musrif, Mr SV Shinde, Mr Ram M Dharmkare and Mr Amit Kumar for their cooperation in preparation of manuscript of the book. Special thanks are due to my wife Mrs Purnima Sharma for her valuable cooperation in my life and for sharing a major part of the responsibility of family affairs, so that I could spend my time for this book. I am deeply grateful to my family members who always have been a source of inspiration and happiness for me. I am highly thankful to CBS Publishers & Distributors, New Delhi, and the National Book Trust, India, New Delhi, for bringing out this book nicely and in time. The last, but not the least, I am heartily grateful to the learned reviewers of the original manuscript for their positive and encouraging comments.

Suresh Chandra

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I. Thermodynamics

The study of statistical mechanics becomes important because of its correlation with the thermodynamics, especially with the second law of thermodynamics, which states about the entropy change in a thermodynamical system. From this law, one may arrive at the conclusion that when a system, with constant volume and energy, is in equilibrium, the entropy is the maximum. In the classical statistics, one can find that such a system is in equilibrium when the total probability is the maximum. Therefore, as suggested by Boltzmann, there appears some relationship between the entropy and the probability. It can then be inferred that the statistics through probability, and the thermodynamics through entropy establish this correlation. Therefore, it becomes reasonable to present a brief discussion of the relevant part of thermodynamics prior to studying the statistical mechanics.

1. First law of thermodynamics

The first law of thermodynamics establishes an equivalence between heat energy and the amount of work done. According to this law, the work can be done by supplying energy in the form of heat. This law can be interpreted that it is impossible to get the work done from any machine without giving it an equivalent amount of energy in any form. Furthermore, an equivalent amount of heat can be produced by doing the work. Obviously, the first law of thermodynamics is merely the law of conservation of energy, where all the forms of energy are accounted for. The first law of thermodynamics may be expressed as

$$\mathrm{d}Q = \mathrm{d}U + \mathrm{d}W$$

where $\mathrm{d}U$ is the change in internal energy, $\mathrm{d}W$ the work done and $\mathrm{d}Q$ the heat supplied.

2. Second law of thermodynamics

The first law of thermodynamics tells that the heat and mechanical work both are inter-convertible. That is, the heat can be converted into work and vice versa. It does not tell about the limitation and condition for this conversion, *i.e.,* how much heat can be converted into work whether the transformation can take place itself or not (the direction of energy transformation). The law specifying the condition of transformation of heat into work is known as the second law of thermodynamics. The second law of thermodynamics is generally stated as the following:

Kelvin's statement: It is impossible to get a continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surroundings.

Clausius statement: It is impossible for a self-acting machine, unaided by any external agency to transfer heat from one body to another at a higher temperature.

Both of these statements of the second law of thermodynamics are equivalent. Violation of one automatically leads to violation of the other. They impart a direction for making a possibility for the energy transformation. For the sake of illustration, let us consider the following examples of an isolated systems:

(i) Free expansion: An ideal gas expands spontaneously from a region of high pressure to a region of low pressure until the pressure becomes uniform.

(ii) Heat conduction: In an ideal gas, the heat conducts spontaneously from a region of high temperature to a region of low temperature until the temperature becomes uniform.

(iii) Diffusion: A solute diffuses spontaneously from a region of high concentration to a region of low concentration until the concentration becomes uniform.

Thus, one can conclude that a system, if left to itself (isolated), changes spontaneously at slow or rapid rate in such a way as to approach a definite final state of equilibrium. In such a process, according to the first law of thermodynamics, the total energy of the system involved remains constant before and after the change. It is important to note the direction in these processes, *i.e.,* from high pressure to low pressure, from high temperature to low temperature, and from high concentration to low concentration. There is thus a direction which allows

a system to come to an equilibrium. However, if we assume that after acquiring equilibrium, the process is reversed then obviously the system, at its own, will not move away from the state of equilibrium unless it is aided by some external agency, *e.g.,* two bodies at the same temperature, being in a state of thermal equilibrium will itself not create temperature difference between them provided one of them is not heated by some external source. This principle which determines the direction for the process to take place is the second law of thermodynamics. For the first law of thermodynamics, it dos not matter how the equilibrium has been attained as the energy of the system remains the same, before and after the equilibrium. Thus, the second law of thermodynamics cannot be derived from the first law of thermodynamics. It requires another thermodynamical parameter for the description and mathematical formulation. This parameter is known as the entropy.

2.1 Entropy and second law of thermodynamics

As mentioned in the preceding section, we require a thermodynamical parameter which has a different value for the initial and final states of an isolated system when a process has taken place, even though the internal energy for the two states remain the same. The entropy is such a variable. It is a definite function of the thermal state of a body and is not affected in any way by the manner in which a particular state is achieved. The change in entropy passing from one state A to another state B is

$$S_B - S_A = \int_A^B \frac{\mathrm{d}Q}{T}$$

where $\mathrm{d}Q$ is the quantity of heat absorbed or ejected at a temperature T in going from state A to state B. It can also be noted that

(i) entropy of a system remains constant during an adiabatic change.

(ii) entropy of a system remains constant in all reversible processes.

(iii) entropy of a system increases in all irreversible processes.

As irreversible processes are continuously occurring in nature, the entropy of the universe is increasing. When the two states A and B, mentioned above, are infinitesimally close to each other then change in entropy $\mathrm{d}S = S_B - S_A$ in going from state A to state B is

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T} \qquad \text{or} \qquad \mathrm{d}Q = T\ \mathrm{d}S$$

It may be considered as a mathematical form of the second law of thermodynamics. On combining the first and second laws of thermodynamics, we get

$$T\ \mathrm{d}S = \mathrm{d}U + \mathrm{d}W$$

Exercise 1. An ideal gas undergoes in a reversible isothermal expansion from a volume V_i to a volume V_f. Calculate the change in entropy of the gas.

Solution: From the first law of thermodynamics, we have

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W = \mathrm{d}Q - p\ \mathrm{d}V$$

In case of an ideal gas, internal energy is a function of temperature T only which in an isothermal process remains constant and therefore, $\mathrm{d}U = 0$. Thus, we have

$$\mathrm{d}Q = p\ \mathrm{d}V$$

Now, a small change in entropy of a system is represented as

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T} = \frac{p\ \mathrm{d}V}{T}$$

For an ideal gas, using

$$pV = \mu RT \qquad \text{or} \qquad p = \frac{\mu RT}{V}$$

we get

$$\mathrm{d}S = \mu R\ \frac{\mathrm{d}V}{V}$$

where μ is the mass of gas in moles and R the universal gas constant. Thus, for the isothermal expansion, the change in entropy is obtained, after integration of this equation, as

$$S_f - S_i = \int_{V_i}^{V_f} \mu R\ \frac{\mathrm{d}V}{V} = \mu R\ \ln\Big(\frac{V_f}{V_i}\Big)$$

As $V_f > V_i$, the entropy of the gas increases. But, the entropy in a reversible process remains constant. Thus, in order to carry out this process, there should be a reservoir at temperature T which is in contact with the system and supplies heat to the gas. Consequently, the entropy of the reservoir decreases by the same amount, $\mu R\ \ln(V_f/V_i)$, so that in this process the entropy of the system does not change.

Exercise 2. Calculate the change in entropy of a system containing 500 gm ice at 0°C which melts (reversibly) into water at the same temperature. The latent heat of melting is 80 cal/gm.

Solution: For the ice to melt reversibly, we must put a heat reservoir whose temperature exceeds 0°C by only a differential amount in contact with it. As the temperature of the reservoir is more than 0°C, ice will melt. Since the process is reversible, we can use the relation

$$S_{water} - S_{ice} = \int_0^Q \frac{\mathrm{d}Q}{T}$$

As the temperature during melting process remains constant at 0°C, we have

$$S_{water} - S_{ice} = \frac{1}{T}\int_0^Q \mathrm{d}Q = \frac{Q}{T}$$

Now, $Q = 500 \times 80 = 4 \times 10^4$ cal. Therefore,

$$S_{water} - S_{ice} = \frac{Q}{T} = \frac{4 \times 10^4}{273} = 146.5 \text{ cal/K}$$

Exercise 3. 500 gm of water is heated from 35°C to 85°C. Calculate the change in entropy of water. The specific heat of water has a constant value 4.2 J/gm °C.

Solution: Consider that a process is carried out reversibly by heating water through the baths of steadily increasing temperature. Then the change in entropy of water is

$$\mathrm{d}S = \int_{T_1}^{T_2} \frac{\mathrm{d}Q}{T} = ms\int_{T_1}^{T_2} \frac{\mathrm{d}T}{T}$$

where the relation $\mathrm{d}Q = ms\ \mathrm{d}T$ is used. Here, m is the mass and s the specific heat of the material. Thus, we have

$$\mathrm{d}S = ms\ \ln\Big(\frac{T_2}{T_1}\Big) = 500 \times 4.2 \times \ln\Big(\frac{358}{308}\Big) = 315.91 \text{ J/K}$$

Exercise 4. (a) 1000 gm of water at 0°C is brought into contact with a large heat reservoir at 100°C. The temperature of water increases slowly from 0°C to 100°C. Calculate the change in entropy of water and of the reservoir. (b) If the water is heated from 0°C to 100°C 35°C, first by bringing in contact of a reservoir at 50°C and then in contact of a

reservoir at 100°C, calculate the change in entropy of the entire system. The specific heat of water has a constant value 4.2 J/gm °C.

Solution: (a) The change in entropy of water when it is heated from 0°C to 100°C is

$$\mathrm{d}S_{water} = ms\,\ln\Big(\frac{T_2}{T_1}\Big) = 1000 \times 4.2 \times \ln\Big(\frac{373}{273}\Big) = 1310.85\ \mathrm{J/K}$$

The entropy lost by the reservoir is

$$\mathrm{d}S_{res} = \frac{\mathrm{d}Q}{T}$$

where $\mathrm{d}Q$ is the heat gained by water heated up to 100°C. Thus,

$$\mathrm{d}Q = ms\ \Delta t = 1000 \times 4.2 \times (100 - 0) = 4.2 \times 10^5\ \mathrm{J}$$

Thus,

$$\mathrm{d}S_{res} = \frac{4.2 \times 10^5}{373} = 1126.0\ \mathrm{J/K}$$

Hence, the change in energy of the entire system is

$$\mathrm{d}S_{sys} = 1310.85 - 1126.0 = 184.85\ \mathrm{J/K}$$

(b) In this case, the entropy gained by the water is

$$\mathrm{d}S_{water} = ms\Big[\ln\Big(\frac{T_2}{T_1}\Big) + \ln\Big(\frac{T_2}{T_2}\Big)\Big] = ms\,\ln\Big(\frac{T_3}{T_1}\Big)$$

$$= 1000 \times 4.2 \times \ln\Big(\frac{373}{273}\Big) = 1310.85\ \mathrm{J/K}$$

It shows that the entropy gained is the same as in case (a). Now, the entropy lost by the first reservoir is

$$\mathrm{d}S_{res1} = \frac{\mathrm{d}Q_1}{T_1} = \frac{ms\Delta t_1}{T_1} = \frac{1000 \times 4.2 \times (50 - 0)}{273 + 50} = 650.15\ \mathrm{J/K}$$

The entropy lost by the second reservoir is

$$\mathrm{d}S_{res2} = \frac{\mathrm{d}Q_2}{T_2} = \frac{ms\Delta t_2}{T_2} = \frac{1000 \times 4.2 \times (100 - 50)}{273 + 100} = 563.00\ \mathrm{J/K}$$

Hence, the change in entropy of the entire system is

$$\mathrm{d}S_{sys} = 1310.85 - 650.15 - 563.00 = 97.7\ \mathrm{J/K}$$

It shows the change in entropy of the entire system decreases when the water is heated with the help of two reservoirs at different temperatures.

Exercise 5. 500 gm of ice at 100 K is converted to superheated steam at 500 K at a pressure of 10^5 N/m^2. Calculate the change in entropy of water. Specific heat at constant pressure of ice, liquid and vapour are, respectively, 2.09 $\times 10^3$, 4.2 $\times 10^3$ and 2.09 $\times 10^3$ J/kg K. The latent heat for vapourization = 2.26 $\times 10^5$ J/kg and the latent heat for fusion = 8.34 $\times 10^5$ J/kg.

Solution: (i) Change in entropy of 0.5 kg of ice for change of temperature from 100 K to 273 K is

$$\mathrm{d}S_1 = ms\,\ln\Big(\frac{T_2}{T_1}\Big) = 0.5 \times 2.09 \times 10^3 \times \ln\Big(\frac{273}{100}\Big) = 1049.5 \text{ J/K}$$

(ii) Change in entropy of 0.5 kg of ice at 0°C when changes to water at 0°C is

$$\mathrm{d}S_2 = \frac{mL}{T} = \frac{0.5 \times 8.34 \times 10^5}{273} = 1527.48 \text{ J/K}$$

(iii) Change in entropy of 0.5 kg of water for change of temperature from 0°C to 100°C is

$$\mathrm{d}S_3 = ms\,\ln\Big(\frac{T_2}{T_1}\Big) = 0.5 \times 4.18 \times 10^3 \times \ln\Big(\frac{373}{273}\Big) = 652.30 \text{ J/K}$$

(iv) Change in entropy of 0.5 kg of water at 100°C when changes to steam at 100°C is

$$\mathrm{d}S_4 = \frac{mL}{T} = \frac{0.5 \times 2.26 \times 10^5}{373} = 302.95 \text{ J/K}$$

(v) Change in entropy of 0.5 kg of steam for change of temperature from 373 K to 500K is

$$\mathrm{d}S_5 = ms\,\ln\Big(\frac{T_2}{T_1}\Big) = 0.5 \times 2.09 \times 10^3 \times \ln\Big(\frac{500}{373}\Big) = 306.22 \text{ J/K}$$

Thus, total change in entropy is

$$\mathrm{d}S = 1049.5 + 1527.48 + 652.30 + 302.95 + 306.22 = 3838.63 \text{ J/K}$$

3. Entropy as a measure of disorder

In order to show that the entropy is a measure of disorder, let us consider three states (solid, liquid and gas) of a substance. In a gas, molecules move in a random manner and therefore, we cannot specify the arrangement of the molecules. Consequently, we say that the gaseous state is a disorderly state. In a liquid state, the molecules do not have as much freedom to move as in the gaseous state and hence, as compared to the gaseous state, liquid state may be considered as less disorderly. In the solid state, arrangement of molecules can be specified as they are held by the intermolecular forces and therefore, the solid state may be considered as an orderly state. Hence, we find that when a substance is converted from solid to liquid and then from liquid to gas, the degree of disorder increases successively. At the same time, it is also obvious that in the process of the change of state from solid to liquid and then liquid to gas, the entropy increases. Hence, with the increase of the degree of disorder, the entropy increases. Converse is also true. When the steam is converted into water and then into ice, the entropy and the degree of disorder of the molecules decreases. Thus, we can say that the entropy is a measure of disorder.

4. Disorder is the most probable state

It is the law of nature that disorder is always more probable than the order. There is probability for an orderly state to transform to a disorderly state but it is highly improbable that a highly disordered motion of molecules of a single body would by itself be converted into a regular motion like that of the engine shaft, say. Gamow, about this transformation of order and disorder, quotes the example that every army officer knows that a disorganized group of men is a natural state of affairs while an organized team of men is unnatural state and requires a lot of organizing activity.

Thus, it is the law of nature that disorder is always more probable than order and as the entropy is a measure of disorder, it is obvious that in a process in which there is an increase in entropy, disorderly state is more probable.

5. Statistical definition of entropy

We have noted that disorderly state is highly probable to occur during the course of a natural process. It shows that occurrence of disorderly

state is closely concerned with the law of probability. The equilibrium state is the state of maximum entropy thermodynamically and the state of the most probable statistically. It will be shown further that the disorder of a system may be calculated by the theory of probability and expressed by a quantity known as the thermodynamic probability or the disorder. It would be shown in classical statistics that the relation between the entropy S and the probability W is

$$S = k \ln W$$

where k is the Boltzmann constant. It would also be recognized that W is the number of states accessible to the system. Following the quantum statistics, it would be shown that when the macrostate of a system is specified, W is completely determined. It will then enable to calculate the entropy of the system.

Exercise 6. For one mole of ideal gas in a quasi-static process, the heat absorbed $\mathrm{d}Q$ is expressed as $\mathrm{d}Q = c_V \, \mathrm{d}T + \overline{p} \, \mathrm{d}V$, where $\mathrm{d}T$ is the change in the temperature, $\mathrm{d}V$ the change in the volume, c_V the constant molar specific heat at constant volume, and $\overline{p}$ the mean pressure, expressed as $\overline{p} = RT/V$. Obtain an expression for the change in the entropy of the gas when the initial values of temperature and volume, T_i and V_i change to the final values T_f and V_f, respectively.

Solution: Using the relations

$$\mathrm{d}Q = T \, \mathrm{d}S \qquad \text{and} \qquad \overline{p} = \frac{RT}{V}$$

in the given expression $\mathrm{d}Q = c_V \, \mathrm{d}T + \overline{p} \, \mathrm{d}V$, we get

$$T \, \mathrm{d}S = c_V \, \mathrm{d}T + \frac{RT}{V} \, \mathrm{d}V \qquad \text{or} \qquad \mathrm{d}S = c_V \, \frac{\mathrm{d}T}{T} + R \, \frac{\mathrm{d}V}{V}$$

When the system goes from the initial state i to the final state f, we have

$$\int_{S_i}^{S_f} \mathrm{d}S = c_V \int_{T_i}^{T_f} \frac{\mathrm{d}T}{T} + R \int_{V_i}^{V_f} \frac{\mathrm{d}V}{V}$$

On integration, we get

$$S_f - S_i = c_V \, \ln\Big(\frac{T_f}{T_i}\Big) + R \, \ln\Big(\frac{V_f}{V_i}\Big)$$

This is the required expression.

6. Thermodynamic potentials

Thermodynamical variables such as pressure P, volume V, temperature T, and entropy S define the state of a thermodynamical system. A relation between them exists because of the first and second laws of thermodynamics, respectively, expressed as

$$\mathrm{d}Q = \mathrm{d}U + P\ \mathrm{d}V \qquad \text{and} \qquad \mathrm{d}Q = T\ \mathrm{d}S$$

On combining these relations, we get

$$\mathrm{d}U = T\ \mathrm{d}S - P\ \mathrm{d}V$$

Any two of these four variables, P, V, T, S, are independent and then with the help of the above relations, the remaining variables can be determined. For full description of a thermodynamical phenomenon, other relations among these variables are required. These relations are knows as the thermodynamic potentials. There are four such potentials as the following.

6.1 Internal energy

In a system, as the molecules are moving, they have kinetic energy. Further, because of interaction between the molecules, there is potential energy. The sum of the kinetic energy and potential energy is known as the total internal energy of the system. This internal energy is independent of the path followed by the system in arriving at a final state f from an initial state i. It is the function of initial and final states only. Suppose $\mathrm{d}Q$ is the amount of heat absorbed by the system and $\mathrm{d}W$ is the work done by the system in arriving from the initial state i to the final state f, then

$$U_f - U_i = \mathrm{d}U = \mathrm{d}Q - \mathrm{d}W$$

where $\mathrm{d}U$ is the change in internal energy of the system between the two states. Using the relations

$$\mathrm{d}Q = T\ \mathrm{d}S \qquad \text{and} \qquad \mathrm{d}W = P\ \mathrm{d}V$$

we get

$$\mathrm{d}U = T\ \mathrm{d}S - P\ \mathrm{d}V \tag{1.1}$$

Equation (1.1) gives

$$\Big(\frac{\partial U}{\partial V}\Big)_S = -P \qquad \text{and} \qquad \Big(\frac{\partial U}{\partial S}\Big)_V = T \tag{1.2}$$

Since

$$\frac{\partial}{\partial S}\Big(\frac{\partial U}{\partial V}\Big) = \frac{\partial}{\partial V}\Big(\frac{\partial U}{\partial S}\Big)$$

Using the above expressions (1.2) for P and T, we get

$$\Big(\frac{\partial P}{\partial S}\Big)_V = -\Big(\frac{\partial T}{\partial V}\Big)_S$$

6.2 Helmholtz function F

On combining the first and second laws of thermodynamics, we have

$$\mathrm{d}U = T\ \mathrm{d}S - \mathrm{d}W$$

Suppose the temperature of the system remains constant, then $\mathrm{d}(TS) = T\ \mathrm{d}S$ and we have

$$\mathrm{d}U = \mathrm{d}(TS) - \mathrm{d}W \qquad \text{or} \qquad \mathrm{d}(U - TS) = -\mathrm{d}W$$

The function F, expressed as

$$F = U - TS \tag{1.3}$$

is known as the Helmholtz function or Helmholtz free energy. Thus, we have

$$\mathrm{d}F = -\mathrm{d}W$$

It shows that in a reversible isothermal process, the work done by the system is equal to the decrease in Helmholtz free energy. On account of this fact, F is also known as the work function. On differentiating equation (1.3), we get

$$\mathrm{d}F = \mathrm{d}U - T\ \mathrm{d}S - S\ \mathrm{d}T$$

Using equation (1.1) here, we get

$$\mathrm{d}F = -P\ \mathrm{d}V - S\ \mathrm{d}T \tag{1.4}$$

Equation (1.4) gives

$$\Big(\frac{\partial F}{\partial T}\Big)_V = -S \qquad \text{and} \qquad \Big(\frac{\partial F}{\partial V}\Big)_T = -P \tag{1.5}$$

Since

$$\frac{\partial}{\partial V}\Big(\frac{\partial F}{\partial T}\Big) = \frac{\partial}{\partial T}\Big(\frac{\partial F}{\partial V}\Big)$$

Using the above expressions (1.5) for S and P, we get

$$\Big(\frac{\partial S}{\partial V}\Big)_T = \Big(\frac{\partial P}{\partial T}\Big)_V$$

Note: Form equation (1.3), we find that TS is $U - F$ and is known as the latent energy or bound energy of the system. Thus, the relation $U = F + TS$ can be interpreted as

Intrinsic energy = Helmholtz free energy + Latent energy

6.3 Enthalpy H

Thermodynamical phenomena at constant pressure are expressed in terms of another function called the enthalpy or heat content of the system, expressed as

$$H = U + PV$$

On differentiating this equation, we get

$$\mathrm{d}H = \mathrm{d}U + P\ \mathrm{d}V + V\ \mathrm{d}P$$

Using equation (1.1) here, we get

$$\mathrm{d}H = T\ \mathrm{d}S + V\ \mathrm{d}P \tag{1.6}$$

When the process is carried out at constant pressure, we have

$$\mathrm{d}H = T\ \mathrm{d}S = \mathrm{d}Q$$

Hence, the enthalpy represents the quantity of heat given to the system from an external source and hence the name heat content. Equation (1.6) gives

$$\Big(\frac{\partial H}{\partial P}\Big)_S = V \qquad \text{and} \qquad \Big(\frac{\partial H}{\partial S}\Big)_P = T \tag{1.7}$$

Since

$$\frac{\partial}{\partial S}\Big(\frac{\partial H}{\partial P}\Big) = \frac{\partial}{\partial P}\Big(\frac{\partial H}{\partial S}\Big)$$

Using the above expressions (1.7) for V and T, we get

$$\Big(\frac{\partial V}{\partial S}\Big)_P = \Big(\frac{\partial T}{\partial P}\Big)_S$$

6.4 Gibbs potential G

Suppose the thermodynamic process is isothermal ($\mathrm{d}T = 0$) and isobaric ($\mathrm{d}P = 0$), then from equation (1.6), we have

$$\mathrm{d}H = T\ \mathrm{d}S = \mathrm{d}(TS) \qquad \text{or} \qquad \mathrm{d}(H - TS) = 0 \qquad \text{or} \qquad \mathrm{d}G = 0$$

where

$$G = H - TS = U + PV - TS \tag{1.8}$$

is known as the Gibbs free energy. On differentiating equation (1.8), we get

$$\mathrm{d}G = \mathrm{d}U + P\ \mathrm{d}V + V\ \mathrm{d}P - T\ \mathrm{d}S - S\ \mathrm{d}T$$

Using equation (1.1) here, we get

$$\mathrm{d}G = V\ \mathrm{d}P - S\ \mathrm{d}T \tag{1.9}$$

Equation (1.9) gives

$$\Big(\frac{\partial G}{\partial P}\Big)_T = V \qquad \text{and} \qquad \Big(\frac{\partial G}{\partial T}\Big)_P = -S \tag{1.10}$$

Since

$$\frac{\partial}{\partial T}\Big(\frac{\partial G}{\partial P}\Big) = \frac{\partial}{\partial P}\Big(\frac{\partial G}{\partial T}\Big)$$

Using the above expressions (1.10) for V and S, we get

$$\Big(\frac{\partial V}{\partial T}\Big)_P = \Big(\frac{\partial S}{\partial P}\Big)_T$$

7. Thermodynamic equilibriums

A system is said to be in equilibrium when its state does not change with time. Depending on the concerned physical parameter, we can have various types of equilibriums: (i) Mechanical equilibrium, (ii) Chemical equilibrium, (iii) Thermal equilibrium. Here, we would like to express the conditions of a thermodynamical equilibrium of a system in terms of thermodynamic functions. Let us consider a system A in contact with the surrounding B (*e.g.,* in case of air contained in a vessel, the air is the system A and the vessel behaves as the surrounding B). There is an exchange of heat between them due to which there would be change in their entropies. Let these changes in A and B be denoted by $\mathrm{d}S_A$ and

$\mathrm{d}S_B$, respectively. Then from the second law of thermodynamics (law of increase of entropy), we have

$$\mathrm{d}S_A + \mathrm{d}S_B \geq 0 \tag{1.11}$$

where inequality sign shows the increase in entropy for an irreversible process and equality sign shows no change in entropy for a reversible process. Suppose during the process of exchange of heat, system A absorbs a quantity $\mathrm{d}Q$ from surrounding B. We may take B as a reservoir at constant temperature T so that it can be safely assumed that heat is absorbed from it in a reversible manner. In such a case, we have

$$\mathrm{d}S_B = -\frac{\mathrm{d}Q}{T}$$

From the first law of thermodynamics, we have

$$\mathrm{d}Q = (\mathrm{d}U + \mathrm{d}W)_A \qquad \text{or} \qquad -T\ \mathrm{d}S_B = (\mathrm{d}U + \mathrm{d}W)_A$$

Therefore,

$$\mathrm{d}S_B = -\frac{(\mathrm{d}U + \mathrm{d}W)_A}{T}$$

and from equation (1.11), we have

$$\mathrm{d}S_A - \frac{(\mathrm{d}U + \mathrm{d}W)_A}{T} \geq 0$$

As a general condition, we write as (by dropping the suffix A)

$$\mathrm{d}S - \frac{\mathrm{d}U + \mathrm{d}W}{T} \geq 0 \tag{1.12}$$

Here, we have

$$T\ \mathrm{d}S - \mathrm{d}U - \mathrm{d}W > 0 \qquad \text{for an irreversible process}$$

and

$$T\ \mathrm{d}S - \mathrm{d}U - \mathrm{d}W = 0 \qquad \text{for a reversible process}$$

7.1 Adiabatic equilibrium

In this case $\mathrm{d}Q = 0$ as the system is thermally isolated from its surroundings, and therefore

$$\mathrm{d}Q = \mathrm{d}U + \mathrm{d}W = 0$$

Then from equation (1.12), we have

$$\mathrm{d}S \geq 0$$

As the entropy of an isolated system tends to increase, it goes on increasing till equilibrium is attained. Thus, at the equilibrium, the entropy becomes the maximum. Hence, at the equilibrium, we have

$$\mathrm{d}S = 0 \qquad \text{or} \qquad S = S_{max}$$

In other words, the state of stable adiabatic equilibrium is characterized by an absolute maximum of the entropy.

7.2 Isothermal equilibrium

Here, we shall discuss two cases, separately.

(i) Isochoric process

In this process, the volume of the gas remains constant. For such a process $\mathrm{d}W = 0$ so that from equation (1.12), we have

$$T\ \mathrm{d}S - \mathrm{d}U \geq 0 \qquad \text{or} \qquad \mathrm{d}U - T\ \mathrm{d}S \leq 0$$

As the temperature T is constant, we have

$$\mathrm{d}U - \mathrm{d}(TS) \leq 0 \qquad \text{or} \qquad \mathrm{d}(U - TS) \leq 0 \qquad \text{or} \qquad \mathrm{d}F \leq 0$$

Since in a natural change, Helmholtz free energy F always decreases, the equilibrium will be obtained when it becomes the minimum. Also there exists the minimum of F beyond which the change is no loner possible, so that

$$\mathrm{d}F = 0$$

(ii) Isobaric process

In this process, the pressure P of the gas remains constant, so that $\mathrm{d}W = P\ \mathrm{d}V = \mathrm{d}(PV)$ and from equation (1.12), we have

$$T\ \mathrm{d}S - \mathrm{d}U - \mathrm{d}(PV) \geq 0$$

As T is constant, we have

$$\mathrm{d}(U + PV - TS) \leq 0 \qquad \text{or} \qquad \mathrm{d}G \leq 0$$

Since in a natural change, Gibbs free energy G always decreases, the equilibrium will be obtained when it becomes the minimum. Also there exists the minimum of G beyond which the change is no loner possible, so that

$$\mathrm{d}G = 0$$

8. Problems and questions

1. Discuss in brief about the thermodynamic potentials.
2. Discuss in brief about the thermodynamic equilibriums.
3. Write notes on the following

    (i) First law of thermodynamics
    (ii) Second law of thermodynamics
    (iii) Entropy and second law of thermodynamics
    (iv) Entropy as a measure of disorder
    (v) Entropy are most probable states
    (vi) Statistical definition of entropy
    (vii) Intrinsic energy of a thermodynamical system
    (viii) Helmholtz function of a thermodynamical system
    (ix) Enthalpy of a thermodynamical system
    (x) Gibbs potential of a thermodynamical system
    (xi) Adiabatic equilibrium
    (xii) Isochoric process
    (xiii) Isobaric process

II. Fundamentals

In statistical mechanics, we deal with the physical systems comprising a large number ($\sim 10^{23}$) of identical particles. The simplest system of our interest is a perfect gas in thermal equilibrium. From the macroscopic point of view, a physical system appears as a continuous one. But, from the microscopic point of view, it consists of discrete particles (atoms or molecules). For treatment of a system, we consider both the macroscopic as well as microscopic states of it. Let us first introduce about the macroscopic and microscopic states of a system.

1. Macroscopic and microscopic states

Let us consider a physical system comprising a large number N of identical particles (atoms or molecules) which are moving freely from one place to another within the system. Here, we shall consider structureless identical particles. Thus, it does not matter whether the gas consists of atoms or molecules. Since the particles enjoy free movement, thus the interaction between them should be very weak (it is zero in an ideal case) and therefore, the separations between them should be large. The particles, which are enormous in number, would obviously occupy a large volume V. A typical number of particles in a system is of the order of 10^{23}. Though the values of N and V are enormously large, the particle density

$$\rho = \frac{N}{V}$$

in a system however has a finite value. Total energy E of the system is equal to the sum of the energies ϵ_i of individual particles comprising the system

$$E = \sum_i n_i \epsilon_i$$

where n_i is the number of particles having equal energy ϵ_i. Total number N of the particles in the system is therefore

$$N = \sum_i n_i$$

Here, we have assumed that the energy of the particles is discrete (quantized). However, in the classical mechanics, energy of the particles is continuous, and then we have

$$N = \int n(\epsilon)\, \mathrm{d}\epsilon \qquad \text{and} \qquad E = \int \epsilon\, n(\epsilon)\, \mathrm{d}\epsilon$$

where $n(\epsilon)\, \mathrm{d}\epsilon$ is the number of particles having energy in the range from ϵ to $\epsilon + \mathrm{d}\epsilon$. When the spacing between the energy levels is small, the energy may be treated to be continuous.

From the macroscopic point of view, a state of a system is described by a number N of the constituent particles, its volume V and energy E. The energy is related to the kinetic temperature T and the number of constituent particles is basically related to the mass m of the system. Thus, N, V, E, T, m are the parameters related to the macrostate of the system. In this scenario, we however do not get any knowledge about the position and momentum coordinates of the constituent particles. The macroscopic parameters (N, V, E) provide knowledge about the system which is obtained by averaging over all the constituent particles.

In the microscopic consideration, information about the constituent particles of the system is taken into account. Now, a state of the system is defined by the position coordinates q and momentum coordinates p of the constituent particles. For a system of N particles, here, q represents a set of $3N$ position coordinates, q_1, q_2, ..., q_{3N} and p represents a set of $3N$ momentum coordinates, p_1, p_2, ..., p_{3N}. For one set of position and momentum coordinates, the system is represented by one point in the phase space.[1] Such state of the system is known as a microscopic state or microstate.

For a given macrostate (*i.e.,* for the given values of N, V and E of the system) there are a large number of microstates (as the position and momentum coordinates of the constituent particles are changing continuously). Thus, from the microscopic point of view, the macroscopic description of the system is not applicable. Therefore, a microstate of a macroscopically defined system is described through a probability density $\rho(q, p, t)$ which is a function of position and momentum coordinates of the constituent particles and time t.

Activity 1:

In order to understand about the macrostate and microstate of a system, let us look into an example. A female child is born in a common family and she was named Anshika. Anshika was a good looking girl.

[1]Phase space is described in the following section, it is the space where position and momentum coordinates are taken as independent coordinates of the space.

The family has been fond of taking her photo on her birth-day each year. This habit continued even when she was grown up and got married. In the family of her in-laws also, she was liked by each and every member, and there also the process of snapping her photo on each of her birth-day continued. Her children also continued to take her snap on her birth-day every year. In this example, Anshika as a person and her parents signify the macrostate, which remained unchanged through out her life. Her size, look, activities and views etc. describe the microstate, which went on developing with time. Here, each photo corresponds to one microstate.

2. Phase space

Let us consider a physical system comprising a large number N of identical particles (atoms or molecules) which are moving freely from one place to another within the system. Suppose, the energy and volume of the system are E and V, respectively. A macrostate of the system is described by N, V and E. For a given macrostate of a system, there are a large number of microstates as the position and momentum coordinates of the constituent particles are changing continuously with time. A microstate of a system comprising N particles is defined by $3N$ position coordinates, q_1, q_2, ..., q_{3N} and $3N$ momentum coordinates, p_1, p_2, ..., p_{3N}. This $6N$-dimensional space is known as the 'phase space' of the system. If the system is in the gaseous condition, the phase space is also known as the Γ-space.[2] A point (q, p), where q represents a set of position coordinates q_1, q_2, ..., q_{3N} and p represents a set of momentum coordinates p_1, p_2, ..., p_{3N}, in the phase space, called a phase point (Figure 1a), represents a microstate. With the passage of time, position and momentum coordinates of the constituent particles change continuously and therefore, the phase point moves in the phase space, generating a phase line (also called, a phase trajectory) (Figure 1b).

A locus of phase points in the phase space such that the total energy E of the system remains constant defines a surface, called the energy surface of energy E. For a given macrostate, trajectory of the phase point always lies on the energy surface as the energy of the system is constant. If the total energy of the system lies in the range from E to $E+\mathrm{d}E$, the trajectory of the space points would lie within the shell

[2]In classical mechanics, we use two different approaches, expressed by the Lagrangian $L(q, \dot{q}, t)$ and the Hamiltonian $H(q, p, t)$. Remember that in the Hamiltonian, q and p are treated as independent coordinates. Obviously, the Hamiltonian approach deals in the phase space.

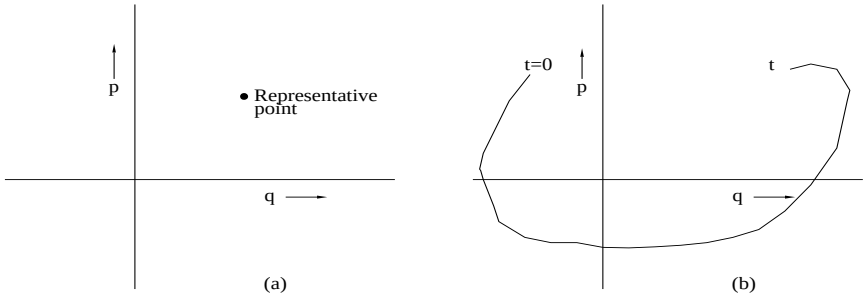

Figure 1: Representative point (phase point) in the phase space of the system is shown in (a). It represents one microstate of the system. Microstate of the system changes with time and therefore, position of phase point varies with time. Trajectory (phase line) of the representative point is shown in (b)

described by the range of the energy (Figure 2).

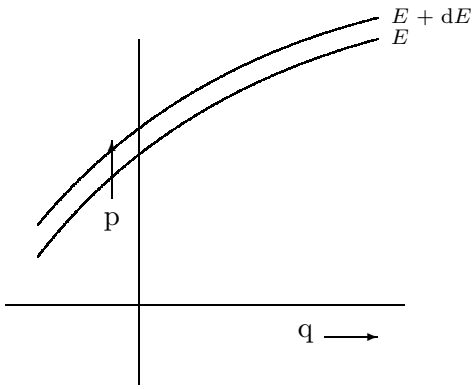

Figure 2: Two energy surfaces corresponding to the energies E and $E + \mathrm{d}E$ in the phase space are shown.

Exercise 1. A particle is moving freely in three-dimensional space. Find the number of coordinates of the particle in the phase space.

Solution: A particle moving freely in the three-dimensional space is described by the space coordinates q_1, q_2, q_3 and momentum components p_1, p_2, p_3. Thus, in the phase space, the particle has six coordinates q_1, q_2, q_3, p_1, p_2, p_3.

Exercise 2. A particle is moving freely in a two-dimensional plane. Find the number of coordinates of the particle in the phase space.

Solution: A particle moving freely in two-dimensional space is described by the space coordinates q_1, q_2 and momentum components p_1, p_2. Thus, in the phase space, the particle has four coordinates q_1, q_2, p_1, p_2.

3. Ensemble and ensemble average

For a system of identical particles which are moving freely from one place to another, we can set up equations of motion and solve them to calculate the time average of a physical quantity of interest. For a large number of particles in the system, the equations of motion are enormous in number. Hence, to find out their solution is a quite cumbersome task; it is almost impossible. Around 1900 Gibbs suggested a way out of getting rid of these equations of motion by introducing the concept of an ensemble for calculating average value of the physical quantity for the system. The concept of an ensemble can be understood in the following manner.

Each point in a phase space develops out of the previous one in time. Hence, with the passage of time t, a system goes through various microstates (represented by the phase points) though the macrostate of the system remains unchanged. Gibbs introduced a noble idea to replace this time dependent picture (Figure 3a) by a static one in which all the phase points are supposed to exist simultaneously at one time (Figure 3b).

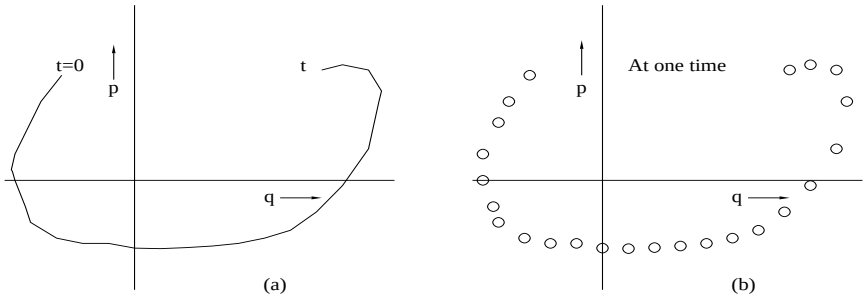

Figure 3: A phase line is shown in (a) where various points represent different microstates of the system of interest, developed with the passage of time. Macrostate of the system is the same, described by N, V and E. Gibbs considered the entire phase line to exist at one time as shown in (b), where only a limited number of actual phase points is shown. In fact, the phase points are continuous and are very large in number.

A collection of these simultaneously existing imaginary systems (Fig-

ure 4) is known as an ensemble.[3] In the ensemble, the elements are replica of the actual system of interest where microstate differs from one to another, but the macrostate remains unchanged. The number M of the elements in an ensemble is enormously large. The elements of an ensemble being imaginary do not interact with one another.

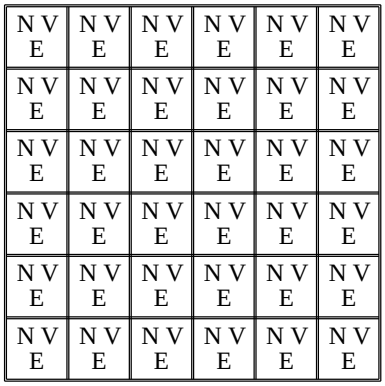

Figure 4: Collection of simultaneously existing Gibbs points, which correspond to different microstates of the system, is known as an 'ensemble'. Macrostate of all these elements of the ensemble is the same described by N, V and E. A limited number of elements of the ensemble are shown here. In fact, the number of elements is enormously large

Now, instead of taking time average of a physical quantity of the system which is evolving with time, we can take average over an ensemble of the system where the elements are existing at one time simultaneously. This process of averaging a physical quantity over the ensemble is known as the ensemble average[4].

For calculating the ensemble average of a physical quantity, let us consider a physical system comprising a large number N of identical particles (atoms or molecules) which are moving freely from one place to another within the system. Ensemble average of a physical quantity is expressed in terms of a density function $P(q, p, t)$, where q represents a set of position coordinates q_1, q_2, ..., q_{3N}, p represents a set of momentum coordinates p_1, p_2, ..., p_{3N}, in the phase space, and t the time.

[3]In the activity 1, discussed earlier, suppose we put all the snaps of Anshika, taken on her birth-day each year, together at one place. This collection of snaps is an ensemble, which were taken on different times, but now have been put together.

[4]It is difficult to prove the exact equivalence between the 'time average' and the 'ensemble average'. However, one can hope the equivalence between the two averages when the number of the constituent particles in a system is very large ($N \to \infty$) and the number of elements in the ensemble is also very large ($M \to \infty$).

This function P represents the number density of phase points in the phase space. Thus, the number of phase points in the volume element $\mathrm{d}q\ \mathrm{d}p$ is

$$\mathrm{d}q\ \mathrm{d}p \equiv \mathrm{d}q_1\ \mathrm{d}q_2\ \ldots\ \mathrm{d}q_{3N}\ \mathrm{d}p_1\ \mathrm{d}p_2\ \ldots\ \mathrm{d}p_{3N}$$

around a point (q, p) in the phase space is $P(q, p, t)\ \mathrm{d}q\ \mathrm{d}p$. Therefore, the total number of phase points in the phase space (which is equal to the number M of the elements in the ensemble of the system) is

$$\int P(q, p, t)\ \mathrm{d}q\ \mathrm{d}p = M$$

The normalized density function, denoted by $\rho(q, p, t)$ and called as the probability density, is

$$\rho(q, p, t) = \frac{P(q, p, t)}{M}$$

Obviously, the probability density satisfies the normalization condition

$$\int \rho(q, p, t)\ \mathrm{d}q\ \mathrm{d}p = 1$$

This function $\rho(q, p, t)$ is also known as the statistical distribution function or simply the distribution function of the system. Now the probability $\mathrm{d}W$ of finding phase points in the volume element $\mathrm{d}q\ \mathrm{d}p$ around the point (q, p) in the phase space is

$$\mathrm{d}W = \rho(q, p, t)\ \mathrm{d}q\ \mathrm{d}p$$

The ensemble average $\langle f \rangle$ of a physical quantity $f(q, p)$ is

$$\langle f \rangle = \int f(q, p)\ \rho(q, p, t)\ \mathrm{d}q\ \mathrm{d}p$$

In general, the ensemble average $\langle f \rangle$ is a function of time. However, when the ensemble represents a system in equilibrium, the probability density does not depend on time explicitly. That is

$$\frac{\partial \rho}{\partial t} = 0$$

Then the ensemble average $\langle f \rangle$ is independent of time. Such an ensemble is said to be stationary.

Activity 2:

Suppose we want to study about the life cycle of a star. Stars are born; they grow and enjoy their life and then die out. Life span of a

star is billions of years and we cannot go so long. (Average age of a person may be about 80 years or so.) The life style of a star depends on its mass. A very high-mass star ends its life in the form of a black-hole and the elements produced inside the star may be up to iron (Fe); A low-mass star ends its life in the form of a white dwarf and the elements inside are produced up to helium (He) only. A star having intermediate mass end its life in the form of a neutron star. In the universe, we have billions of galaxies and each galaxy may have billions of stars having various masses and various ages.

Suppose we want to study the life style of a star having mass which is (say) five times more than that of the sun. Then, we select the stars having the same mass but different ages. This collection of stars having different ages but the same mass is an ensemble. Here, the equal mass of the stars describes the macrostate. With the age of a star, formation of elements and other processes are going on inside the stars and they form the microstates. The information about some physical quantity about a star can be calculated by taking the average of the quantity over this ensemble.

4. Liouville's theorem

In the phase space, distribution of phase points is expressed by the probability density $\rho(q, p, t)$ (which also describes an ensemble at any instant). This function $\rho(q, p, t)$, in general, changes with time due to the motion of phase points in the phase space. Liouville's theorem states that the probability density $\rho(q, p, t)$ is constant along the phase trajectories of the phase points. It is also known as the principle of conservation of the probability density in phase space and can be mathematically expressed as

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$$

Proof of this theorem can be given in the following manner. Let us consider a physical system comprising a large number N of identical particles. For the $6N$-dimensional phase space of the system, let q represents a set of position coordinates q_1, q_2, ..., q_{3N}, and p represents a set of the momentum coordinates p_1, p_2, ..., p_{3N}. Consider a volume element $\mathrm{d}q\ \mathrm{d}p \equiv \mathrm{d}q_1\ \mathrm{d}q_2\ \ldots\ \mathrm{d}q_{3N}\ \mathrm{d}p_1\ \mathrm{d}p_2\ \ldots\ \mathrm{d}p_{3N}$ around a point (q, p) in the phase space. The number $\mathrm{d}M$ of phase points in the volume element is $\mathrm{d}M = \rho(q, p, t)\ \mathrm{d}q\ \mathrm{d}p$. The number of phase points in the volume element will, in general, change with time due to the motion of the phase points. The change will occur when the number of phase

points entering the volume element is different from those leaving the volume element.

Let us consider a motion of phase points along the q_1-axis. For that, we consider two faces A and B normal to the q_1-axis at the coordinates q_1 and $q_1 + \mathrm{d}q_1$, respectively (Figure 5). Suppose, the phase points are entering at the face A and are leaving at the face B.

(i) At the face A:

Velocity of the phase points along the q_1-axis is $\dot{q_1}$.

Let the probability density be ρ.

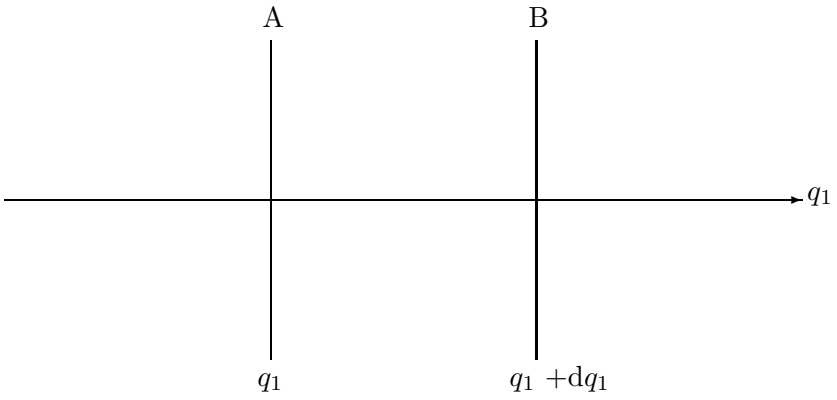

Figure 5: Faces A and B are normal to the q_1-axis at the positions q_1 and $q_1 + \mathrm{d}q_1$, respectively.

Hence, the number of phase points entering the face A per unit area in time $\mathrm{d}t$ is $\rho\, \dot{q_1}\, \mathrm{d}t$.

(ii) At the face B:

Velocity of the phase points along the q_1-axis is

$$\Big(\dot{q_1} + \frac{\partial \dot{q_1}}{\partial q_1}\, \mathrm{d}q_1 \Big)$$

The probability density is

$$\Big(\rho + \frac{\partial \rho}{\partial q_1}\, \mathrm{d}q_1 \Big)$$

Hence, the number of phase points leaving the face B per unit area in time $\mathrm{d}t$ is

$$\Big(\rho + \frac{\partial \rho}{\partial q_1}\, \mathrm{d}q_1 \Big) \Big(\dot{q_1} + \frac{\partial \dot{q_1}}{\partial q_1}\, \mathrm{d}q_1 \Big)\, \mathrm{d}t$$

Hence, the net number of phase points entering the region between the faces A and B per unit area in time $\mathrm{d}t$ is

$$= \rho\, \dot{q_1}\ \ \mathrm{d}t - \Big(\rho + \frac{\partial \rho}{\partial q_1}\ \mathrm{d}q_1\Big)\Big(\ \dot{q_1} + \frac{\partial \dot{q_1}}{\partial q_1}\ \mathrm{d}q_1\Big)\ \mathrm{d}t$$

$$= -\Big(\rho\ \frac{\partial \dot{q_1}}{\partial q_1} + \dot{q_1}\ \frac{\partial \rho}{\partial q_1}\Big)\mathrm{d}q_1\ \mathrm{d}t$$

Here, higher order term is neglected. When the separation between the faces A and B is unit (*i.e.,* $\mathrm{d}q_1 = 1$) , the number of phase points entering the region between the faces A and B per unit volume in time $\mathrm{d}t$ is

$$-\Big(\rho\ \frac{\partial \dot{q_1}}{\partial q_1} + \dot{q_1}\ \frac{\partial \rho}{\partial q_1}\Big)\ \mathrm{d}t$$

Similarly, for the motion of phase points along the p_1-axis, the net number of phase points entering the region per unit volume in time $\mathrm{d}t$ is

$$-\Big(\rho\ \frac{\partial \dot{p_1}}{\partial p_1} + \dot{p_1}\ \frac{\partial \rho}{\partial p_1}\Big)\ \mathrm{d}t$$

After accounting for all the $6N$ coordinates of the phase space, the net number of phase points entering the region per unit volume in time $\mathrm{d}t$ is

$$= -\sum_{i=1}^{3N}\Big[\Big(\rho\frac{\partial \dot{q_i}}{\partial q_i} + \dot{q_i}\ \frac{\partial \rho}{\partial q_i}\Big)\ \mathrm{d}t + \Big(\rho\frac{\partial \dot{p_i}}{\partial p_i} + \dot{p_i}\ \frac{\partial \rho}{\partial p_i}\Big)\ \mathrm{d}t\Big]$$

$$= -\sum_{i=1}^{3N}\Big[\rho\Big(\frac{\partial \dot{q_i}}{\partial q_i} + \frac{\partial \dot{p_i}}{\partial p_i}\Big) + \frac{\partial \rho}{\partial q_i}\ \dot{q_i} + \frac{\partial \rho}{\partial p_i}\ \dot{p_i}\ \Big]\ \mathrm{d}t \qquad (2.1)$$

For the Hamiltonian $H(q,p)$ of the system, the equations of motion are

$$\dot{q_i} = \frac{\partial H}{\partial p_i} \qquad \text{and} \qquad \dot{p_i} = -\frac{\partial H}{\partial q_i} \qquad i = 1, 2, \ldots, 3N$$

Thus, we have

$$\frac{\partial \dot{q_i}}{\partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} \qquad \text{and} \qquad \frac{\partial \dot{p_i}}{\partial p_i} = -\frac{\partial^2 H}{\partial p_i \partial q_i}$$

and therefore,

$$\frac{\partial \dot{q_i}}{\partial q_i} + \frac{\partial \dot{p_i}}{\partial p_i} = 0$$

Using this relation in equation (2.1), the net number of phase points entering the region per unit volume in time dt is

$$-\sum_{i=1}^{3N}\Big[\frac{\partial\rho}{\partial q_i}\,\dot{q}_i+\frac{\partial\rho}{\partial p_i}\,\dot{p}_i\Big]\,\mathrm{d}t \tag{2.2}$$

The change of phase points per unit volume in time dt is

$$=\frac{1}{\mathrm{d}q\mathrm{d}p}\,\frac{\partial}{\partial t}(\rho\mathrm{d}q\mathrm{d}p)\,\mathrm{d}t=\frac{\partial\rho}{\partial t}\mathrm{d}t \tag{2.3}$$

From equations (2.2) and (2.3), we have

$$\frac{\partial\rho}{\partial t}\,\mathrm{d}t=-\sum_{i=1}^{3N}\Big[\frac{\partial\rho}{\partial q_i}\,\dot{q}_i+\frac{\partial\rho}{\partial p_i}\,\dot{p}_i\Big]\,\mathrm{d}t$$

Since dt is not zero, we get

$$\frac{\partial\rho}{\partial t}+\sum_{i=1}^{3N}\Big[\frac{\partial\rho}{\partial q_i}\,\dot{q}_i+\frac{\partial\rho}{\partial p_i}\,\dot{p}_i\Big]=0 \tag{2.4}$$

$$\frac{\partial\rho}{\partial t}+\sum_{i=1}^{3N}\frac{\partial\rho}{\partial q_i}\frac{\mathrm{d}q_i}{\mathrm{d}t}+\sum_{i=1}^{3N}\frac{\partial\rho}{\partial p_i}\frac{\mathrm{d}p_i}{\mathrm{d}t}=0$$

$$\frac{\mathrm{d}\rho}{\mathrm{d}t}=0$$

It proves the Liouville's theorem. An ensemble for which $\rho(q,p,t)$ is constant along the trajectories in the phase space is known as a stationary ensemble. This corresponds to an equilibrium situation.

(i) Case of steady state

For the steady state state, we have $\partial\rho/\partial t=0$, and equation (2.4) can be written as

$$\sum_{i=1}^{3N}\Big[\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i}-\frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i}\Big]=0 \qquad \text{or} \qquad \sum_{i=1}^{3N}\Big[\frac{\partial\rho}{\partial q_i}\,\dot{q}_i+\frac{\partial\rho}{\partial p_i}\,\dot{p}_i\Big]=0$$

$$\text{or} \qquad \vec{V}.\,\mathrm{grad}\rho=0$$

where

$$\vec{V}=\sum_{i=1}^{3N}\Big[\,\dot{q}_i\,\hat{q}_i+\dot{p}_i\;\hat{p}_i\Big] \qquad \text{and} \qquad \mathrm{grad}\rho=\sum_{i=1}^{3N}\Big[\frac{\partial\rho}{\partial q_i}\,\hat{q}_i+\frac{\partial\rho}{\partial p_i}\,\hat{p}_i\Big]$$

in the phase space. Hence, the system moves on a surface of constant ρ. Thus, when ρ is explicitly independent of time, it should also be independent of the coordinates (q, p). That is

$$\rho(q, p) = \text{constant}$$

Hence, the phase points are uniformly distributed over the relevant region of the phase space and outside the relevant region, ρ is zero.

5. Density matrix

Let us consider a system comprising a large number of identical particles. At any time t, the state of the system is completely described by the wave function Ψ, which can be expressed in terms of the normalized wave functions ψ_n as[5]

$$\Psi = \sum_n c_n(t)\psi_n \tag{2.5}$$

The wave functions ψ_n are time-independent and satisfy the condition of orthonormalization

$$\int \psi_m^* \psi_n \, \mathrm{d}\tau = \delta_{mn}$$

where ψ_m^* is complex conjugate of ψ_m, $\mathrm{d}\tau$ represents the volume element and the expansion coefficient c_n, which is a function of time, is

$$c_n = \int \psi_n^* \Psi \, \mathrm{d}\tau$$

For normalization of the wave functions Ψ we have

$$\int \Psi^* \Psi \, \mathrm{d}\tau = 1$$

$$\int \sum_n c_n^* \, \psi_n^* \sum_m c_m \, \psi_m \, \mathrm{d}\tau = 1$$

[5]Here, ψ_n are the basic functions and the wave function Ψ for a system can be expressed in terms of these basic functions. This may be understood in the following manner. For example, in India, we have currency notes of 1, 2, 5, 10, 20, 50, 100, 500, 1000 rupees. Now suppose, we want to give Rs. 5858 to some one. We can give as

$5846 = 5 \times 1000 + 1 \times 500 + 3 \times 100 + 2 \times 20 + 1 \times 5 + 1 \times 1$

Let the notes of 1, 2, 5, 10, 20, 50, 100, 500, 1000 rupees, be denoted respectively by ψ_1, ψ_2, ψ_3, ψ_4, ψ_5, ψ_6, ψ_7, ψ_8, ψ_9. We can obviously take $\Psi = 5856$. On writing

$$\Psi = \sum_{i=1}^{9} c_i \psi_i$$

Then, we get $c_1 = 1$, $c_2 = 0$, $c_3 = 1$, $c_4 = 0$, $c_5 = 2$, $c_6 = 0$, $c_7 = 3$, $c_8 = 1$, $c_9 = 5$.

$$\sum_n \sum_m c_n^* \; c_m \int \psi_n^* \; \psi_m \; \mathrm{d}\tau = 1$$

Thus,

$$\sum_n c_n^* \; c_n = 1 \qquad \text{or} \qquad \sum_n |c_n|^2 = 1$$

Mean value of a quantity f of the system in this state is

$$\langle f \rangle = \int \Psi^* \hat{f} \Psi \; \mathrm{d}\tau \tag{2.6}$$

where $\hat{f}$ is an operator corresponding to f. Using equation (2.5) in (2.6), we get

$$\langle f \rangle = \int \sum_n c_n^* \psi_n^* \hat{f} \sum_m c_m \psi_m \; \mathrm{d}\tau = \sum_n \sum_m c_n^* c_m \int \psi_n^* \hat{f} \psi_m \; \mathrm{d}\tau \tag{2.7}$$

$$= \sum_n \sum_m c_n^* c_m f_{nm}$$

where f_{nm} defined as

$$f_{nm} = \int \psi_n^* \; \hat{f} \; \psi_m \; \mathrm{d}\tau = \langle n | \hat{f} | m \rangle$$

is a matrix elements of the quantity f, which corresponds to the transition from the state n to the state m. Defining

$$\rho_{mn} = c_n^* c_m \tag{2.8}$$

we have

$$\langle f \rangle = \sum_m \sum_n \rho_{mn} f_{nm}$$

The quantities ρ_{mn} form a matrix known as the density matrix in the energy representation. The elements ρ_{mn} of the matrix are, in general, functions of time.

If we assume that ρ_{mn} is a transition element of some statistical operator $\hat{\rho}$, then by using the matrix multiplication, we have

$$\sum_n \rho_{mn} f_{nm} = \sum_n \langle m | \hat{\rho} | n \rangle \langle n | \hat{f} | m \rangle = \langle m | \hat{\rho} \hat{f} | m \rangle$$

which is a diagonal element of the matrix of the operator $(\hat{\rho}\hat{f})$. Then, we have

$$\langle f \rangle = \sum_m \sum_n \rho_{mn} f_{nm} = \sum_m \langle m | \hat{\rho} \hat{f} | m \rangle = \mathrm{tr}(\hat{\rho} \hat{f}) \tag{2.9}$$

5.1 Normalization condition for density matrix

Putting $\hat{f} = 1$ in equation (2.7) gives

$$\langle f \rangle = \sum_n \sum_m c_n^* c_m \int \psi_n^* \psi_m \, \mathrm{d}\tau = \sum_n c_n^* c_n = 1$$

Further, $f_{nm} = \delta_{nm}$ and therefore, from equation (2.9), we get

$$\mathrm{tr}(\hat{\rho}) = \sum_m \rho_{mm} = 1$$

which is the normalization condition for the density matrix.

5.2 Time derivative of density matrix

Now, we are interested in finding out time derivative of the density matrix. For the wave function Ψ in equation (2.5), ψ_n is independent of time, but the expansion coefficient c_n is a function of time, which can be expressed as

$$c_n(t) = c_n(0) \, \exp(-iE_n t/\hbar)$$

where $c_n(0)$ is the value of the expansion coefficient at $t = 0$. We have

$$c_n^*(t) c_m(t) = c_n^*(0) c_m(0) \, \exp\Big[i(E_n - E_m)t/\hbar\Big]$$

Thus,

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\Big(c_n^*(t) c_m(t)\Big) &= c_n^*(0) c_m(0) \, \exp\Big[i(E_n - E_m)t/\hbar\Big] \, \frac{i}{\hbar}(E_n - E_m) \\ &= \frac{i}{\hbar}(E_n - E_m) \; c_n^*(t) \; c_m(t) \end{aligned} \tag{2.10}$$

Using equation (2.8) in (2.10), we have

$$\frac{\mathrm{d}\rho_{mn}}{\mathrm{d}t} = \frac{i}{\hbar}(E_n - E_m)\rho_{mn} = \frac{i}{\hbar}\Big[\rho_{mn} E_n - E_m \rho_{mn}\Big]$$

It can be expressed as[6]

[6]We have

$$H_{ln} = \int \psi_l^* \hat{H} \psi_n \, \mathrm{d}\tau = E_n \int \psi_l^* \psi_n \, \mathrm{d}\tau \qquad \text{Thus,} \qquad H_{nn} = E_n$$

and

$$H_{ml} = \int \psi_m^* \hat{H} \psi_l \, \mathrm{d}\tau = E_l \int \psi_m^* \psi_l \, \mathrm{d}\tau \qquad \text{Thus,} \qquad H_{mm} = E_m$$

$$\frac{\mathrm{d}\rho_{mn}}{\mathrm{d}t} = \frac{i}{\hbar}\sum_{l}\Big[\rho_{ml}H_{ln} - H_{ml}\rho_{ln}\Big]$$

where H_{mn} are the matrix elements of the Hamiltonian $\hat{H}$ of the system. Thus,

$$i\hbar\,\frac{\mathrm{d}\rho_{mn}}{\mathrm{d}t} = \sum_{l}\Big[\langle m|\hat{H}|l\rangle\langle l|\hat{\rho}|n\rangle - \langle m|\hat{\rho}|l\rangle\langle l|\hat{H}|n\rangle\Big]$$

$$= \langle m|\hat{H}\hat{\rho}|n\rangle - \langle m|\hat{\rho}\hat{H}|n\rangle = \langle m|\hat{H}\hat{\rho} - \hat{\rho}\hat{H}|n\rangle$$

When $\mathrm{d}\rho_{mn}/\mathrm{d}t = 0$, we have

$$\langle m|\hat{H}\hat{\rho} - \hat{\rho}\hat{H}|n\rangle = 0 \qquad \text{or} \qquad \hat{H}\hat{\rho} = \hat{\rho}\hat{H}$$

It shows that when $\mathrm{d}\rho_{mn}/\mathrm{d}t = 0$, the operator $\hat{\rho}$ commutes with the energy operator $\hat{H}$.

Exercise 3. Find out coordinate representation of density matrix $\rho = \exp(-\beta H)$, where $H = p^2/2m$ and $\beta = 1/kT$, for a free particle of mass m. When the wave function of the particle is periodic in a cube having each side of length L, calculate its limiting value for $L \to \infty$. [The wave function being periodic satisfies the conditions: $\psi(x, y, z) = \psi(x + L, y, z)$; $\psi(x, y, z) = \psi(x, y + L, z)$; $\psi(x, y, z) = \psi(x, y, z + L)$.]

Solution: Schrödinger equation for a free particle of mass m

$$-\frac{\hbar^2}{2m}\Big(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\Big)\psi = E\psi$$

for energy E has a solution[7]

$$\psi(x, y, z) = \frac{1}{\sqrt{L^3}}\,\exp[i(k_x x + k_y y + k_z z)]$$

where

$$k_x^2 = \frac{2m}{\hbar^2}\,E_x \qquad k_y^2 = \frac{2m}{\hbar^2}\,E_y \qquad k_z^2 = \frac{2m}{\hbar^2}\,E_z$$

Here, E_x, E_y and E_z are components of energy such that $E = E_x + E_y + E_z$. In order to satisfy the boundary conditions (*i.e.,* periodicities: $\psi(x, y, z) = \psi(x + L, y, z)$; $\psi(x, y, z) = \psi(x, y + L, z)$; $\psi(x, y, z) = \psi(x, y, z + L)$.) we have

$$k_x L = 2\pi n_x \qquad k_y L = 2\pi n_y \qquad k_z L = 2\pi n_z$$

[7]Solution is taken from the Quantum Mechanics.

where n_x, n_y and n_z are integers and the energy is

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\ (k_x^2 + k_y^2 + k_z^2) = \frac{h^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

For the known eigen values and eigen functions, the coordinate representation $\langle\ \vec{r}\,'\ |\rho|\ \vec{r}\ \rangle$ of the density matrix ρ is

$$\langle\ \vec{r}\ |\rho|\ \vec{r}\,'\ \rangle = \sum_E \psi^*(\vec{r}\,')\ \mathrm{e}^{-\beta E}\psi(\vec{r})$$

Using the eigen values and eigen functions of the particle, we get

$$\langle\ \vec{r}\,'\ |\rho|\ \vec{r}\ \rangle = \sum_{n_x=-\infty}^{\infty}\sum_{n_y=-\infty}^{\infty}\sum_{n_z=-\infty}^{\infty}\frac{1}{L^3}\ \exp\Big[-\frac{\beta h^2}{2mL^2}(n_x^2+n_y^2+n_z^2)$$
$$+\frac{2\pi i}{L}\Big\{n_x(x-x')+n_y(y-y')+n_z(z-z')\Big\}\Big]$$

This equation can be resolved into three parts, one involving x, second y and the third z, as

$$\langle\ \vec{r}\,'\ |\rho|\ \vec{r}\ \rangle = \langle x'|\rho_x|x\rangle\ \langle y'|\rho_y|y\rangle\ \langle z'|\rho_z|z\rangle$$

where

$$\langle x'|\rho_x|x\rangle = \sum_{n_x=-\infty}^{\infty}\frac{1}{L}\ \exp\Big[-\frac{\beta h^2 n_x^2}{2mL^2}+\frac{2\pi i}{L}n_x(x-x')\Big]$$

In the limit, $L\to\infty$, we have

$$\sum_{n_x=-\infty}^{\infty}\frac{1}{L}\to\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}k_x \qquad \Big(k_x=\frac{2\pi}{L}\ n_x\Big)$$

and thus, we have[8]

$$\langle x'|\rho_x|x\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}k_x\ \exp\Big[-\frac{\beta h^2}{2m}k_x^2+ik_x(x-x')\Big]$$

[8] We have

$$\int_{-\infty}^{\infty}\exp\Big(-\frac{a}{2}x^2+ibx\Big)\mathrm{d}x = \int_{-\infty}^{\infty}\exp\Big(-\frac{1}{2}a\Big[x-\frac{ib}{a}\Big]^2-\frac{b^2}{2a}\Big)\mathrm{d}x$$
$$= \mathrm{e}^{-b^2/2a}\int_{-\infty}^{\infty}\exp\Big(-\frac{a}{2}\Big[x-\frac{ib}{a}\Big]^2\Big)\mathrm{d}x = \sqrt{\frac{2\pi}{a}}\ \mathrm{e}^{-b^2/2a}$$

$$= \Big(\frac{m}{2\pi\beta\hbar^2}\Big)^{1/2} \exp\Big[-\frac{m}{2\beta\hbar^2}(x-x')^2\Big]$$

Similarly, we get

$$\langle y'|\rho_y|y\rangle = \Big(\frac{m}{2\pi\beta\hbar^2}\Big)^{1/2} \exp\Big[-\frac{m}{2\beta\hbar^2}(y-y')^2\Big]$$

and

$$\langle z'|\rho_z|z\rangle = \Big(\frac{m}{2\pi\beta\hbar^2}\Big)^{1/2} \exp\Big[-\frac{m}{2\beta\hbar^2}(z-z')^2\Big]$$

On combining these three relations, we get

$$\langle\ \vec{r}'\ |\rho|\ \vec{r}\ \rangle = \Big(\frac{m}{2\pi\beta\hbar^2}\Big)^{1/2} \exp\Big[-\frac{m}{2\beta\hbar^2}(\vec{r}-\vec{r}')^2\Big]$$

This the required coordinate representation of the density matrix.

Exercise 4. Find out x-representation of the density matrix $\rho = \exp(-\beta H)$, where $H = p^2/2m + m\omega^2 x^2/2$ and $\beta = 1/kT$, for a one-dimensional harmonic oscillator. Discuss the limiting case for $\beta\hbar\omega << 1$.

Solution: Schrödinger equation for the linear harmonic oscillator

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2m}{\hbar^2}\Big(E - \frac{1}{2}m\omega^2 x^2\Big)\psi = 0$$

with the eigenvalue $E_n = (n+1/2)\hbar\omega$ has eigen function[9]

$$\psi_n(x) = \Big(\frac{m\omega}{\pi\hbar}\Big)^{1/4} \frac{H_n(y)}{\sqrt{2^n n!}}\ \mathrm{e}^{-y^2/2} \qquad \text{with} \qquad y = \sqrt{\frac{m\omega}{\hbar}}\ x$$

The Hermite polynomial $H_n(y)$ are defined as

$$H_n(y) = (-1)^n\ \mathrm{e}^{y^2}\ \Big(\frac{\partial}{\partial y}\Big)^n \mathrm{e}^{-y^2} = \frac{\mathrm{e}^{y^2}}{\sqrt{\pi}}\ \int_{-\infty}^{\infty} (-2iu)^n\ \mathrm{e}^{-u^2+2iyu}\mathrm{d}u$$

For the known eigen values and eigen functions, the x-representation $\langle x'|\rho|x''\rangle$ of the density matrix ρ is

$$\langle x'|\rho|x''\rangle = \langle x'|\mathrm{e}^{-\beta\ H}|x''\rangle = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta E_n}\ \psi_n(x')\ \psi_n(x'')$$

[9]Solution is taken from the Quantum Mechanics.

Using integral form for the Hermite polynomials, we get

$$\langle x'|\mathrm{e}^{-\beta H}|x''\rangle = \Big(\frac{m\omega}{\pi\hbar}\Big)^{1/2}\frac{\mathrm{e}^{(y'^2+y''^2)/2}}{\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\sum_{n=0}^{\infty}\frac{(-2uv)^n}{n!}$$

$$\times\ \mathrm{e}^{-(n+1/2)\beta\hbar\omega}\ \mathrm{e}^{(-u^2+2iy'u)}\ \mathrm{e}^{(-v^2+2iy''v)}\mathrm{d}u\ \mathrm{d}v$$

Using the relation

$$\sum_{n=0}^{\infty}\frac{(-2uv)^n}{n!}\mathrm{e}^{-n\beta\hbar\omega} = \sum_{n=0}^{\infty}\frac{[-2uv\ \exp(-\beta\hbar\omega)]^n}{n!} = \mathrm{e}^{-2uv\ \exp\{-\beta\hbar\omega\}}$$

the integrand is

$$\mathrm{e}^{-\beta\hbar\omega/2}\mathrm{e}^{[-u^2+2iy'u-v^2+2iy''v-2uv\ \exp(-\beta\hbar\omega)]}$$

Using a general integral formula:

$$\int_{-\infty}^{\infty}\dots\int_{-\infty}^{\infty}\exp\Big(-\frac{1}{2}\sum_{j}^{n}\sum_{k}^{n}a_{jk}x_jx_k + i\sum_{k}^{n}b_kx_k\Big)\mathrm{d}x_1\dots\mathrm{d}x_n$$

$$= \sqrt{\frac{(2\pi)^n}{\det(A)}}\ \exp(-\frac{1}{2}\sum_{j}^{n}\sum_{k}^{n}A^{-1}_{jk}b_jb_k)$$

where A is the matrix (a_{jk}) and A^{-1}_{jk} is an element of the inverse matrix A^{-1}. Here, we have

$$x_1 = u \qquad x_2 = v \qquad b_1 = 2y' \qquad b_2 = 2y''$$

$$a_{11} = a_{22} = 2 \qquad a_{21} = a_{12} = 2\ \exp(-\beta\hbar\omega)$$

Thus, we have

$$A = 2\begin{bmatrix} 1 & \mathrm{e}^{-\beta\hbar\omega} \\ \mathrm{e}^{-\beta\hbar\omega} & 1 \end{bmatrix}$$

so that $\det(A) = 4\ (1 - \mathrm{e}^{-2\beta\hbar\omega})$ and

$$A^{-1} = \tfrac{1}{2(1-\mathrm{e}^{-2\beta\hbar\omega})}\begin{bmatrix} 1 & -\mathrm{e}^{-\beta\hbar\omega} \\ -\mathrm{e}^{-\beta\hbar\omega} & 1 \end{bmatrix}$$

Therefore, we have

$$A^{-1}_{11} = A^{-1}_{22} = \frac{1}{2(1-\mathrm{e}^{-2\beta\hbar\omega})} \quad \text{and} \quad A^{-1}_{21} = A^{-1}_{12} = -\frac{\mathrm{e}^{-\beta\hbar\omega}}{2(1-\mathrm{e}^{-2\beta\hbar\omega})}$$

Applying these values, we get

$$\langle x'|\mathrm{e}^{-\beta\ H}|x''\rangle = \Big(\frac{m\omega}{\pi\hbar}\Big)^{1/2}\frac{\mathrm{e}^{-\beta\hbar\omega/2}}{(1-\mathrm{e}^{-2\beta\hbar\omega})^{1/2}}$$

$$\times\ \exp\Big[\frac{1}{2}(y'^2+y''^2)-\frac{1}{(1-\mathrm{e}^{-2\beta\hbar\omega})}(y'^2-2y'y''\mathrm{e}^{-\beta\hbar\omega}+y''^2)\Big]$$

$$=\Big[\frac{m\omega}{2\pi\hbar\ \sinh(\beta\hbar\omega)}\Big]^{1/2}\ \exp\Big[-\frac{1}{2}(y'^2+y''^2)\ \coth(\beta\hbar\omega)+\frac{y'y''}{\sinh(\beta\hbar\omega)}\Big]$$

Using

$$\tanh(\beta\hbar\omega/2)=\frac{\sinh(\beta\hbar\omega)}{1+\cosh(\beta\hbar\omega)}$$

we get

$$\langle x'|\mathrm{e}^{-\beta\ H}|x''\rangle = \Big[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\Big]^{1/2}$$

$$\times\ \exp\Big[-\frac{m\omega}{4\hbar}\Big\{(x'+x'')^2\ \tanh(\beta\hbar\omega/2)+(x'-x'')^2\ \coth(\beta\hbar\omega/2)\Big\}\Big]$$

Limiting case:

When $\beta\hbar\omega << 1$, $\sinh(\beta\hbar\omega)\to\beta\hbar\omega$ and $\tanh(\beta\hbar\omega/2)\to\beta\hbar\omega/2$, and we have

$$\langle x'|\mathrm{e}^{-\beta\ H}|x''\rangle = \Big[\frac{m}{2\pi\hbar^2\beta}\Big]^{1/2}\exp\Big[-\frac{\beta m\omega^2}{8}(x'+x'')^2-\frac{m}{2\beta\hbar^2}(x'-x'')^2\Big]$$

This is the required x-representation of the density matrix.

6. Fluctuations in a physical quantity

In statistical mechanics, what we measure is the mean value of a physical quantity. In fact, a physical quantity f, in general, differs from its mean value. A typical variation of the physical quantity f and its mean value $\langle f\rangle$ are shown in Figure 6. Here, we have assumed the variation of $\langle f\rangle$ to be smooth and continuous.

Fluctuation of the physical quantity from its mean value is

$$\Delta f = f-\langle f\rangle$$

Thus, the mean fluctuation is

$$\langle\Delta f\rangle = \Big\langle f-\langle f\rangle\Big\rangle = \langle f\rangle-\langle f\rangle = 0$$

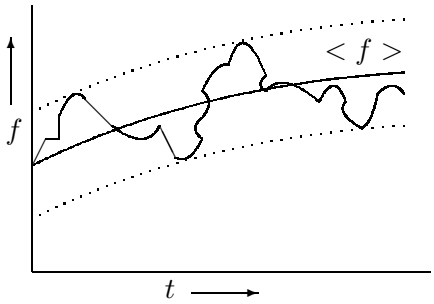

Figure 6: True value of the physical quantity f is shown by the irregular line whereas its mean value $\langle f \rangle$ is shown by the solid continuous line.

The mean square fluctuation is

$$\left\langle (\Delta f)^2 \right\rangle = \left\langle \Big(f - \langle f \rangle \Big)^2 \right\rangle = \left\langle f^2 + \langle f \rangle^2 - 2f\langle f \rangle \right\rangle$$

$$= \langle f^2 \rangle + \langle f \rangle^2 - 2\langle f \rangle\langle f \rangle = \langle f^2 \rangle - \langle f \rangle^2$$

7. Problems and questions

1. Explain macrostate and microstate of a gas. State the parameters which describe the macrostate and microstate of the system.

2. A microstate of a system is defined by f position coordinates and f momentum coordinates of the constituent particles. The degrees of freedom of the system are:

   (i) f (ii) $2f$ (iii) $3f$ (iv) $6f$

   Ans. (i)

3. For a system of a large number of identical particles, the concept of ensemble average was introduced by

   (i) Planck (ii) Kelvin (iii) Hamilton (iv) Gibbs

   Ans. (iv)

4. State and prove Liouville's theorem.

5. Show that in a steady state, probability density is independent of the coordinates of the phase space.

6. Discuss about the density matrix. Obtain normalization condition for the density matrix.

7. Show that when the time-derivative of density matrix is zero, the density operator $\hat{\rho}$ commutes with the energy operator $\hat{H}$.

8. When the time derivative of density matrix is zero, show that the density matrix operator commutes with the energy operator.

9. Write notes on the following

   (i) Phase space

   (ii) Ensemble and ensemble average

   (iii) Liouville's theorem

   (iv) Density matrix

   (v) Fluctuations in a physical quantity

III. Microcanonical Ensemble

In the preceding chapter, the concept of an ensemble was introduced. When the elements of an ensemble are described by a macrostate given by some constant values of N, V and E, the ensemble is termed as microcanonical ensemble. In such case, the system of interest is isolated form any other systems, and it neither exchanges energy nor particles with the environment. Further, the volume of the system remains constant. Thus, the microcanonical ensemble is an ensemble of isolated system. In the present chapter, we shall discuss about a microcanonical ensemble.

1. Microcanonical distribution

Let us consider a system specified by some constant values of the number of particles N, volume V and energy E. (Let the constant energy of the system be E_0.) The microcanonical ensemble is shown in Figure 1.

N V E_0	N V E_0	N V E_0	N V E_0	N V E_0	N V E_0
N V E_0	N V E_0	N V E_0	N V E_0	N V E_0	N V E_0
N V E_0	N V E_0	N V E_0	N V E_0	N V E_0	N V E_0
N V E_0	N V E_0	N V E_0	N V E_0	N V E_0	N V E_0
N V E_0	N V E_0	N V E_0	N V E_0	N V E_0	N V E_0
N V E_0	N V E_0	N V E_0	N V E_0	N V E_0	N V E_0

Figure 1: Microcanonical ensemble where each element has constant values of the number of particles N, volume V and energy E_0.

The system is isolated and does not exchange energy with any other systems. Since it has a constant energy E_0, the distribution function $\phi(E)$, which is a function of energy, for the system can be defined as

$$\phi(E) = \text{constant} \times \delta(E - E_0)$$

where $\delta(E-E_0)$ is a Dirac delta function which is zero for all the energies, except that when $E = E_0$ (Figure 2). Normalization condition for the distribution function is

$$\int \phi(E)\ \mathrm{d}E = 1$$

The function $\phi(E)$ has a sharp peak at $E = E_0$. However, let it has a small but finite width ΔE_0 so that

$$\phi(E_0)\ \Delta E_0 = 1$$

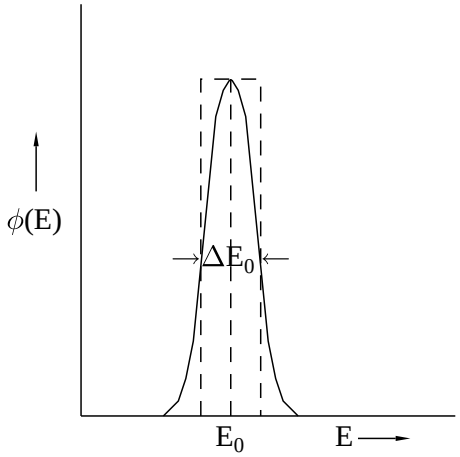

Figure 2: Distribution function $\phi(E)$ as a function of energy E.

The density distribution function in the phase space, which is a function of position and momentum coordinates, in the normalized form may be written as

$$\rho(q, p) = \frac{\delta(E - E_0)}{\Omega(E_0)} \tag{3.1}$$

where $\Omega(E_0)$ is the normalization factor, determined by the normalization condition

$$\int \rho(q, p)\ \mathrm{d}q\ \mathrm{d}p = 1 \tag{3.2}$$

where for a system of N particles, q represents a set of position coordinates q_1, q_2, ..., q_{3N}, p represents a set of momentum coordinates p_1, p_2, ..., p_{3N} and $\mathrm{d}q\ \mathrm{d}p$ is

$$\mathrm{d}q\ \mathrm{d}p \equiv \mathrm{d}q_1\ \mathrm{d}q_2\ \ldots\ \mathrm{d}q_{3N}\ \mathrm{d}p_1\ \mathrm{d}p_2\ \ldots\ \mathrm{d}p_{3N}$$

Using equation (3.1) in (3.2), we get

$$\int \frac{\delta(E-E_0)}{\Omega(E_0)}\ \mathrm{d}q\ \mathrm{d}p = 1 \qquad \text{or} \qquad \Omega(E_0) = \int \delta(E-E_0)\ \mathrm{d}q\ \mathrm{d}p$$

Equation (3.1) is known as the Gibbs microcanonical distribution or simply microcanonical distribution. It shows that all the phase points (and thus, all the elements in the ensemble) have the same energy E_0. This distribution is appropriate for an isolated system where energy of the system is not allowed to change. Hence, the ensemble distributed according to equation (3.1) is known as microcanonical ensemble.

1.1 Microcanonical average

Average of a physical quantity f taken over the microcanonical ensemble is

$$\langle f \rangle = \int f(q,p)\ \rho(q,p)\ \mathrm{d}q\ \mathrm{d}p$$

2. Equal a priori probability

Consider a physical system described by some constant values of the number N of the constituent particles, volume V and energy E. So, the system of interest is defined by the macrostate N, V, E. The system has $6N$-dimensional phase space where each point develops out of the previous one in time. Hence, with the passage of time, a system goes through various microstates (represented by the points in the phase space) though the macrostate of the system remains unchanged. Gibbs introduced a noble idea to replace this time dependent picture by a static one in which all the microstates are considered to exist simultaneously at one time. A collection of these simultaneously existing imaginary systems is known as an ensemble. In the ensemble, the elements are replica of the actual system of interest where microstate differs from one to another, but the macrostate remains unchanged.

A fundamental postulate of statistical mechanics is that a system in equilibrium has equal probability to exist in any of its accessible microstates. It is known as the postulate of 'equal a priori probability'. Though this postulate has no direct proof, but as it does not contradict

any of the known laws of mechanics, it is therefore reasonable to accept this postulate of equal a priori probability.

Hence, following this postulate of equal a priori probability, the number of microstates in a given region of phase space is proportional to the volume of the region. When the phase space is subdivided into cells, each one of a volume h^{3N} (quantum picture),[1] the number of microstates in the given region is proportional to the number of cells in the region.

3. Entropy

Let us consider a system which is divided into a large number of sub-systems, each one of them is isolated from the others. Suppose one of the sub-systems is defined by its total energy E_0, and as it does not interact with the others, its energy distribution function is

$$\phi(E) = \text{constant} \times \delta(E - E_0)$$

which is normalized according to the condition

$$\int \phi(E)\ \mathrm{d}E = 1$$

The probability of finding the sub-system with the energies in the range from E to $E + \mathrm{d}E$ is $\phi(E)\ \mathrm{d}E$. Though $\phi(E)$ is a sharp peaked function around $E = E_0$, it has a small but finite width ΔE_0 so that

$$\phi(E_0)\ \Delta E_0 = 1 \tag{3.3}$$

Let $\Gamma(E)$ denotes the volume of phase space (in classical statistics) and number of quantum states in the phase space (in quantum statistics). It is a dimensionless quantity. In the classical picture Γ can be expressed as

$$\Gamma = \int \mathrm{d}q\ \mathrm{d}p$$

The $\Gamma(E)$ is a function of energy E. Then the volume element (or the number of quantum states) having energies in the range from E to $E+\mathrm{d}E$ can be written as

[1]The volume element is

$$\Delta q_1 \Delta q_2 \ldots \Delta q_{3N} \Delta p_1 \Delta p_2 \ldots \Delta p_{3N}$$

In quantum mechanics, we have $\Delta q_1 \Delta p_1 = h$, $\Delta q_2 \Delta p_2 = h$, $\ldots \Delta q_{3N} \Delta p_{3N} = h$. Thus, the volume element is

$$hh \ldots h = h^{3N}$$

$$\mathrm{d}\Gamma = \frac{\partial \Gamma}{\partial E}\, \mathrm{d}E \tag{3.4}$$

For the density distribution function $\rho(\Gamma)$, the probability that the system has energies in the range from E to $E+\mathrm{d}E$ is

$$\phi(E)\mathrm{d}E = \rho(\Gamma)\, \mathrm{d}\Gamma = \rho(\Gamma)\, \frac{\partial \Gamma}{\partial E}\, \mathrm{d}E$$

where equation (3.4) is used. Thus, the energy distribution function is

$$\phi(E) = \frac{\partial \Gamma(E)}{\partial E}\, \rho(\Gamma(E)) \qquad \text{and} \qquad \phi(E_0) = \frac{\partial \Gamma(E_0)}{\partial E}\, \rho(\Gamma(E_0)) \tag{3.5}$$

Using equation (3.5) in (3.3), we get

$$\frac{\partial \Gamma(E_0)}{\partial E}\, \rho\Big(\Gamma(E_0)\Big)\, \Delta E_0 = 1 \qquad \text{or} \qquad \rho\Big(\Gamma(E_0)\Big)\, \Delta\Gamma = 1$$

where

$$\Delta\Gamma = \frac{\partial \Gamma(E_0)}{\partial E}\, \Delta E_0$$

is the volume element in phase space corresponding to the energy interval ΔE_0. In quantum statistics, $\Delta\Gamma$ is the number of quantum states corresponding to the energy interval ΔE_0. Hence,

$$\Delta\Gamma = \Delta q\, \Delta p$$

Here, the right hand side has a dimension

$$(\text{distance} \times \text{momentum})^{3N}$$

where N is the number of particles in the subsystem. The volume of phase space can be converted into the number of quantum states as

$$\Delta\Gamma = \frac{\Delta q\, \Delta p}{h^{3N}}$$

so that it is a dimensionless quantity. The quantity $\Delta\Gamma$ is defined as statistical weight W of the microstate of the subsystem.

Let us come back to our system which was divided into sub-systems. Suppose, W_1, W_2, ... are statistical weights of the sub-systems. Then the statistical weight W of the system is

$$W = W_1 W_2 \ldots = \prod_i W_i$$

On taking logarithm, we have

$$\ln W = \sum_i \ln W_i \tag{3.6}$$

In statistical mechanics, a relation between the entropy S of an ideal gas and the quantity W, which is the number of microstates corresponding to a given macrostate is

$$S = k \ln W \tag{3.7}$$

where k is the Boltzmann constant. This equation was originally formulated by Boltzmann, but later on put into the current form by Max Planck. This formula is famously displayed on the Boltzmann tombstone, which was erected in the 1930's, at the Central Cemetery, Vienna, Austria. This equation (3.7) gives the statistical definition for entropy. Since the statistical weight can never be less than unity, the entropy cannot be negative.

3.1 Additive property of entropy

Using equation (3.6) in (3.7), we have

$$S = k \sum_i \ln W_i = \sum_i k \ln W_i = \sum_i S_i$$

where $S_i = k \ln W_i$ is the entropy of the i-th sub-system. Hence, the entropy of a system is equal to the sum of the entropies of sub-systems. It is known as the additive property of entropy.

3.2 Derivation of the relation $S = k \ln W$

This relation can be understood in the following manner. According to the first law of thermodynamics, when the internal energy of a system does not change (*i.e.,* the temperature is constant), the heat supplied $\mathrm{d}Q$ is converted completely into the work done W, and we have

$$\mathrm{d}Q = W$$

The work W done by the gas is

$$W = \int_{v_1}^{v_2} P \, \mathrm{d}v$$

where the volume v changes from v_1 to v_2. For an ideal gas, we have

$$Pv = NkT \qquad \text{or} \qquad P = \frac{NkT}{v}$$

where N is the number of particles in the gas. On using the expression for P, we have

$$W = NkT \int_{v_1}^{v_2} \frac{\mathrm{d}v}{v} = NkT \ln\Big(\frac{v_2}{v_1}\Big) = kT \ln\Big(\frac{v_2}{v_1}\Big)^N$$

In the phase space, the volume is $V = v^N$, where v is the volume available to each particle. On substituting the value for W, the heat supplied is

$$\mathrm{d}Q = kT \ln\Big(\frac{V_2}{V_1}\Big) \qquad \text{or} \qquad \frac{\mathrm{d}Q}{T} = k \ln\Big(\frac{V_2}{V_1}\Big)$$

When $\mathrm{d}Q$ is the amount of heat supplied to a system at constant temperature T, the change in entropy ΔS of the system is

$$\Delta S = \frac{\mathrm{d}Q}{T} \qquad \text{and we have} \qquad \Delta S = k \ln\Big(\frac{V_2}{V_1}\Big)$$

Let us assume that the molecules of the gas always spread as uniformly as possible throughout the space available the them. On the so called the principle of uniform spread, the ratio of the probability W_1 that the molecules will all remain in the phase volume V_1, to the probability W_2 of their occupying uniformly a larger phase volume V_2 which is made available to them, is expressed as

$$\frac{W_2}{W_1} = \frac{V_2}{V_1} \qquad \text{and therefore} \qquad \Delta S = k \ln\Big(\frac{W_2}{W_1}\Big)$$

If S_1 and S_2 denote the entropies in the two states, we have $\Delta S = S_2 - S_1$, and therefore, we have

$$S_2 - S_1 = k \ln W_2 - k \ln W_1$$

For one state, we have

$$S = k \ln W$$

4. Entropy of a perfect gas in a microcanonical ensemble

Let us consider a perfect gas having N particles, each one of mass m, confined in a volume V. Suppose the total energy of the system lies in a narrow range from $(E - \mathrm{d}E)$ to E. Volume of the system in the phase space is

$$\int \mathrm{d}q_1 \, \mathrm{d}q_2 \, \ldots \, \mathrm{d}q_{3N} \, \mathrm{d}p_1 \, \mathrm{d}p_2 \, \ldots \, \mathrm{d}p_{3N}$$

where q's and p's are position and momentum coordinates, respectively, of the constituent particles. The corresponding number of quantum states is

$$\Delta\Gamma = \frac{1}{h^{3N}} \int \mathrm{d}q_1 \; \mathrm{d}q_2 \; \ldots \; \mathrm{d}q_{3N} \; \mathrm{d}p_1 \mathrm{d}p_2 \; \ldots \; \mathrm{d}p_{3N} \tag{3.8}$$

In case of a perfect gas (*i.e.,* an ideal gas) considered here, the constituent particles do not interact with one another (*i.e.,* the potential energy of the gas is zero) and thus, the total energy E of the gas is

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

Since, the energy does not depend on the position coordinates of the particles, and the coordinates of a particle are independent of the coordinates of other particles, we have

$$\int \mathrm{d}q_1 \; \mathrm{d}q_2 \; \ldots \; \mathrm{d}q_{3N} = V^N \tag{3.9}$$

Using equation (3.9) in (3.8), we have

$$\Delta\Gamma = \frac{V^N}{h^{3N}} \int \mathrm{d}p_1 \; \mathrm{d}p_2 \; \ldots \; \mathrm{d}p_{3N} \tag{3.10}$$

as the integration over three position coordinates of a particle contributes the volume V of the gas. For the gas, we have a condition

$$(E - \mathrm{d}E) \;\; \leq \;\; \sum_{i=1}^{3N} \frac{p_i^2}{2m} \;\; \leq \;\; E$$

or

$$\left(\sqrt{2m(E - \mathrm{d}E)}\right)^2 \;\; \leq \;\; \left(p_1^2 + p_2^2 + \ldots p_{3N}^2\right) \;\; \leq \;\; \left(\sqrt{2mE}\right)^2$$

Hence, the momentum integral in equation (3.10) is the volume of a hyper-shell having inner and outer radii $\sqrt{2m(E - \mathrm{d}E)}$ and $\sqrt{2mE}$, respectively, in the $3N$-dimensional momentum space. Here, the momentum coordinates of one particle cannot be separated from those of the others. Let us first consider the case of 3-dimensional space, where volume of a spherical shell having inner and outer radii $\sqrt{2m(E - \mathrm{d}E)}$ and $\sqrt{2mE}$, respectively, is

$$\int \mathrm{d}p_1 \; \mathrm{d}p_2 \; \mathrm{d}p_3 = \frac{4\pi}{3}\left(\sqrt{2mE}\right)^3 - \frac{4\pi}{3}\left(\sqrt{2m(E - \mathrm{d}E)}\right)^3$$

$$= \frac{\pi^{3/2}}{\Gamma\Big(\{3+2\}/2\Big)}\Big\{[2mE]^{3/2} - [2m(E-\mathrm{d}E)]^{3/2}\Big\}$$

In analogy, in the $3N$-dimensional momentum space, volume of a hyper-shell having inner and outer radii $\sqrt{2m(E-\mathrm{d}E)}$ and $\sqrt{2mE}$, respectively, is

$$\int \mathrm{d}p_1\ \mathrm{d}p_2\ \ldots\ \mathrm{d}p_{3N} = \frac{\pi^{3N/2}}{\Gamma(\{3N+2\}/2)}\Big\{[2mE]^{3N/2} - [2m(E-\mathrm{d}E)]^{3N/2}\Big\}$$

$$= \frac{(2\pi mE)^{3N/2}}{(3N/2)!}\ \Big\{1 - \Big(1 - \frac{\mathrm{d}E}{E}\Big)^{3N/2}\Big\}$$

$$= \frac{(2\pi mE)^{3N/2}}{(3N/2)!}\ \Big\{1 - \Big[1 - \frac{3N}{2}\frac{\mathrm{d}E}{E} + \frac{1}{2!}\Big(\frac{3N}{2}\Big)\Big(\frac{3N}{2}-1\Big)\Big(\frac{\mathrm{d}E}{E}\Big)^2$$

$$-\frac{1}{3!}\Big(\frac{3N}{2}\Big)\Big(\frac{3N}{2}-1\Big)\Big(\frac{3N}{2}-2\Big)\Big(\frac{\mathrm{d}E}{E}\Big)^3 + \ldots\Big]\Big\}$$

Since N is very large, we can write

$$\int \mathrm{d}p_1\ \mathrm{d}p_2\ \ldots\ \mathrm{d}p_{3N} = \frac{(2\pi mE)^{3N/2}}{(3N/2)!}\ \Big\{1 - \Big[1 - \frac{3N}{2}\frac{\mathrm{d}E}{E}$$

$$+\frac{1}{2!}\Big(\frac{3N}{2}\frac{\mathrm{d}E}{E}\Big)^2 - \frac{1}{3!}\Big(\frac{3N}{2}\frac{\mathrm{d}E}{E}\Big)^3 + \ldots\Big]\Big\}$$

$$= \frac{(2\pi mE)^{3N/2}}{(3N/2)!}\ \Big\{1 - \exp\Big(-\frac{3N}{2}\frac{\mathrm{d}E}{E}\Big)\Big\} = \frac{(2\pi mE)^{3N/2}}{(3N/2)!} \qquad (3.11)$$

Here, we have accounted for the fact that N is very large and therefore, the exponential term is neglected in comparison to 1. Using equation (3.11) in (3.10), we have

$$\Delta\Gamma = \frac{V^N}{h^{3N}}\ \frac{(2\pi mE)^{3N/2}}{(3N/2)!} = \frac{V^N}{(3N/2)!}\ \Big[\frac{(2\pi mE)}{h^2}\Big]^{3N/2}$$

Now, the entropy of the system is

$$S = k\ \ln(\Delta\Gamma) = k\ \ln\Big[\frac{V^N}{(3N/2)!}\Big(\frac{2\pi mE}{h^2}\Big)^{3N/2}\Big]$$

$$= k \ln\Big[V^N\Big(\frac{2\pi mE}{h^2}\Big)^{3N/2}\Big] - k \ln\Big[\Big(\frac{3N}{2}\Big)!\Big]$$

Using Stirling formula, we get,

$$S = k \ln\Big[V^N\Big(\frac{2\pi mE}{h^2}\Big)^{3N/2}\Big] - \frac{3Nk}{2} \ln\Big(\frac{3N}{2}\Big) + \frac{3Nk}{2}$$

$$= kN \ln\Big[V\Big(\frac{2\pi mE}{h^2}\Big)^{3/2}\Big] - Nk \ \ln\Big(\frac{3N}{2}\Big)^{3/2} + \frac{3}{2}\, Nk$$

$$= kN\ln\Big[V\Big(\frac{4\pi mE}{3Nh^2}\Big)^{3/2}\Big] + \frac{3}{2}\, Nk \tag{3.12}$$

This is the expression for entropy of a perfect gas in a microcanonical ensemble.

5. Gibbs paradox

Let us consider a perfect gas having N particles each of mass m, confined in a volume V. Entropy of the gas is given by equation (3.12). In order to check the additive property of entropy of the gas, let us increase each of the volume V, number of particles N, and energy E of the gas by a common factor p, then the entropy S' of the new system (using equation 3.12) is

$$S' = pkN \ln\Big[pV\Big(\frac{pE}{pN}\Big)^{3/2}\Big(\frac{4\pi m}{3h^2}\Big)^{3/2}\Big] + \frac{3}{2}\, pNk$$

$$= pkN \ln\Big[pV\Big(\frac{4\pi mE}{3Nh^2}\Big)^{3/2}\Big] + \frac{3}{2}\, pNk$$

$$= p\Big\{kN \ln\Big[V\Big(\frac{4\pi mE}{3Nh^2}\Big)^{3/2}\Big] + \frac{3}{2}Nk\Big\} + pNk \ln p \tag{3.13}$$

Using equation (3.12) in (3.13), we get

$$S' = pS + pNk \ln p$$

In the new system, particle density $(pN/pV) = N/V$ and the energy per particle $(pE/pN) = E/N$ remain the same as in the old one. Following the additive property of entropy of the gas, the entropy of the new system should be pS. It shows that the entropy given by equation (3.12) does not satisfy the additive property. This is known as the Gibbs paradox.

5.1 Removal of Gibbs paradox

In order to get rid of this paradox, the entropy S of a system is expressed by[2]

$$S = k\ \ln\Big(\frac{\Delta\Gamma}{N!}\Big)$$

It can be noticed that a factor $N!$ is introduced empirically in the denominator of the argument of logarithmic function.[3] We take into account for the fact that the particles are indistinguishable and therefore we divided by $N!$. Hence,

$$S = k\ \ln(\Delta\Gamma) - k\ \ln(N!)$$

Using Stirling formula for $\ln N!$ and equation (3.12) for $k\ \ln(\Delta\Gamma)$, we get

$$S = kN\ \ln\Big[V\Big(\frac{4\pi mE}{3Nh^2}\Big)^{3/2}\Big] + \frac{3}{2}\ Nk - Nk\ \ln\ N + Nk$$

$$= kN\ \ln\Big[\frac{V}{N}\Big(\frac{4\pi mE}{3Nh^2}\Big)^{3/2}\Big] + \frac{5}{2}\ Nk \tag{3.14}$$

Let us now test the additive property of entropy by increasing each of the V, N and E of the gas by a common factor p. The entropy S' of the new system is

$$S' = kpN\ \ln\Big[\frac{pV}{pN}\Big(\frac{pE}{pN}\Big)^{3/2}\Big(\frac{4\pi m}{3h^2}\Big)^{3/2}\Big] + \frac{5}{2}\ pNk$$

$$= p\ \Big\{kN\ \ln\Big[\frac{V}{N}\Big(\frac{4\pi mE}{3Nh^2}\Big)^{3/2}\Big] + \frac{5}{2}\ Nk\Big\} = pS$$

It shows that entropy of the new system is p times the entropy of the old one. It satisfies the additive property of entropy of a perfect gas. Thus, there is no more Gibbs paradox.

Exercise 1. An ideal gas having N particles is contained in a box of volume V. Find the number of states $\Delta\Gamma$ classically and, use it to drive the equation of state. [The volume of a unit sphere in n-dimensional space is $\pi^{N/2}/(n/2)!$.]

[2]This is the same as $\Delta\Gamma$ is expressed as

$$\Delta\Gamma = \frac{V^N}{N!h^{3N}} \int \mathrm{d}p_1\ \mathrm{d}p_2\ \ldots\ \mathrm{d}p_{3N}$$

[3]This is known as the correction for the Boltzmann counting.

Solution: For an ideal gas, the potential energy is zero and thus the total energy of the gas of N particles in a three-dimensional space is

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

The number of states is

$$\Delta\Gamma = \frac{V^N}{N!h^{3N}} \int \mathrm{d}p_1 \; \mathrm{d}p_2 \; \ldots \; \mathrm{d}p_{3N}$$

Following the earlier discussion, we get

$$\Delta\Gamma = \frac{V^N}{N!(3N/2)!} \left(\frac{2\pi mE}{h^2}\right)^{3N/2}$$

There is however a factor of $N!$ required for removal of the Gibbs paradox is included. Now, the entropy of the system is

$$S = k \, \ln(\Delta\Gamma) = k \, \ln\Big[\frac{V^N}{N!(3N/2)!}\Big(\frac{2\pi mE}{h^2}\Big)^{3N/2}\Big]$$

$$= k \, \ln\Big[V^N\Big(\frac{2\pi mE}{h^2}\Big)^{3N/2}\Big] - k \, \ln\Big[\Big(\frac{3N}{2}\Big)!\Big] - k \, \ln N!$$

Using Stirling formula $\ln N! = N \, \ln N - N$, we get

$$S = k \, \ln\Big[V^N\Big(\frac{2\pi mE}{h^2}\Big)^{3N/2}\Big] - \frac{3Nk}{2} \, \ln\Big(\frac{3N}{2e}\Big) - kN \, \ln N + kN$$

$$= kN \, \ln\Big[\frac{V}{N}\Big(\frac{4\pi mE}{3Nh^2}\Big)^{3/2}\Big] + \frac{5}{2} \, Nk$$

Thus, we have

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3}{2} \, \frac{kN}{E} \qquad \text{or} \qquad kT = \frac{2E}{3N} = \frac{2}{3} \, \overline{E}$$

and

$$\frac{P}{T} = \frac{\partial S}{\partial V} = \frac{Nk}{V} \qquad \text{or} \qquad PV = NkT$$

Exercise 2. Consider a system of N oscillators, each of unit mass and having frequency ν. Find the number of states classically and use them to derive a relation between the energy and temperature of the system.

Solution: The Hamiltonian of the system having one-dimensional motion is

$$H = \sum_{i=1}^{N} \Big[\frac{1}{2}\, p_i^2 + \frac{1}{2}\, (2\pi\nu)^2 q_i^2\Big]$$

Hence, the phase integral for one-dimensional motion is

$$\Delta\Gamma = \frac{1}{h^N} \int \mathrm{d}q_1\ \mathrm{d}q_2\ \ldots\ \mathrm{d}q_N\ \mathrm{d}p_1 \mathrm{d}p_2\ \ldots\ \mathrm{d}p_N$$

Using the transformation of variables, $p_i/\sqrt{2} \equiv x_i$ and $2\pi\nu q_i/\sqrt{2} \equiv x_{N+i}$, the Hamiltonian can be expressed as

$$H = \sum_{i}^{2N} x_i^2 \quad \text{and we have} \quad \Delta\Gamma = \frac{1}{(\pi h\nu)^N} \int \mathrm{d}x_1\ \mathrm{d}x_2\ \ldots\ \mathrm{d}x_{2N}$$

This is the volume of $2N$-dimensional sphere with radius E. As discussed in section 4, we get

$$\Delta\Gamma = \frac{1}{(\pi h\nu)^N} \frac{(\pi E)^{2N/2}}{(2N/2)!} = \frac{1}{N!}\, \Big(\frac{E}{h\nu}\Big)^N$$

Now, the entropy of the system is

$$S = k\, \ln(\Delta\Gamma) = k\, \ln\Big[\frac{1}{N!}\, \Big(\frac{E}{h\nu}\Big)^N\Big]$$

Using the Stirling formula, we get

$$S = Nk\, \ln\Big(\frac{E}{h\nu}\Big) - N\, \ln N + N$$

Thus, we have

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{Nk}{E} \qquad \text{or} \qquad E = NkT$$

This is the required relation between the energy E and temperature T.

6. Thermodynamic quantities in a microcanonical ensemble

By rearranging equation (3.14), the energy E of the system can be expressed as

$$E = \frac{3h^2 N^{5/3}}{4\pi m V^{2/3}}\, \exp\Big(\frac{2S}{3Nk} - \frac{5}{3}\Big) \tag{3.15}$$

This expression can be used for deriving expressions for various thermodynamical quantities.

(i) Temperature T of the gas is

$$T = \Big(\frac{\partial E}{\partial S}\Big)_{N,V} = \frac{2E}{3Nk} \qquad \text{or} \qquad E = \frac{3}{2}\, NkT \qquad (3.16)$$

(ii) Average energy per particle $\langle E \rangle$ from equation (3.16) is

$$\langle E \rangle = \frac{E}{N} = \frac{3}{2}\, kT$$

A particle has three degree of freedom. So, the mean kinetic energy of a particle per degree of freedom is $kT/2$.

(iii) Specific heat at constant volume c_V of the system is

$$c_V = \Big(\frac{\partial E}{\partial T}\Big)_V = \frac{3}{2}\, Nk$$

Notice that in the classical treatment, the c_V does not depend on the kinetic temperature T.

7. Sackur-Tetrode formula

Using equation (3.16) in (3.14), the entropy is

$$S = kN\, \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{5}{2}\, Nk$$

This is Sackur-Tetrode formula for entropy of a perfect gas. It is free from the Gibbs paradox. It is the same as the expression for entropy in canonical ensemble.

8. Nernst's heat theorem

This theorem states that at absolute zero of temperature, entropy of a system vanishes, *i.e.,* at $T = 0$, $S = 0$. This is also called the third law of thermodynamics. This theorem can be verified in the following manner. We know that

$$S = k\, \ln(W)$$

where W is the statistical weight of the system, which is a pure number according to quantum statistical mechanics, and k the Boltzmann constant. The statistical weight is a function of energy of the system which increases monotonically with the increase of the temperature of the system.

Hence, when the temperature of the system decreases, its energy decreases and therefore, its statistical weight decreases. When the temperature approaches to the absolute zero, the system must be in the lowest quantum state, *i.e.,* in the ground state where the statistical weight W is equal to unity. Thus, the entropy of the system at the absolute zero temperature vanishes. This is theoretical explanation for the Nernst's theorem. Let us see whether this theorem is satisfied by the Sackur-Tetrode formula for entropy of a perfect gas. Sackur-Tetrode formula for entropy of a perfect gas is

$$S = kN \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{5}{2}\, Nk$$

Substitution of $T = 0$ in this equation does not provide $S = 0$. Hence, the third law of thermodynamics is violated in case of a perfect gas.

9. Problems and questions

1. Which of the three physical parameters remain constant in a system of interest in a microcanonical ensemble:

   N, V, E, T, μ Ans. N, V, E

2. Derive an expression for entropy of a perfect gas in a microcanonical ensemble.

3. What is Gibbs paradox in microcanonical ensemble? How it is removed.

4. Derive Sackur-Tetrode formula for entropy of a perfect gas. Show that (i) it is free from the Gibbs paradox and (ii) it violates the third law of thermodynamics.

5. Derive an expression for specific heat at constant volume c_V of a perfect gas in a microcanonical ensemble.

6. Derive an expression for entropy of an ideal gas in a microcanonical ensemble. Check if it is free from the Gibbs paradox. If not, how to remove the paradox.

7. What is the postulate of equal a priori probability? Why is it acceptable?

8. Gibbs paradox in statistical mechanics is related to

   (A) additive property of energy

(B) additive property of momentum

(C) additive property of entropy

(D) additive property of temperature

Ans. C

9. Write notes on the following

(i) Equal a priori probability

(ii) Entropy of a perfect gas in microcanonical ensemble

(iii) Gibbs paradox in microcanonical ensemble

(iv) c_V of a perfect gas in microcanonical ensemble

(v) Sackur-Tetrode formula for entropy of a perfect gas

(vi) Gibbs microcanonical distribution

IV. Canonical Ensemble

The method of microcanonical ensemble, discussed in the preceding chapter, is applicable only to a system which is perfectly isolated one, as it has constant values for the number of particles N, volume V and energy E. Thus, no exchange of the energy and particles between the system and any external source was feasible. Further, the volume of the system was kept unchanged. We can have a system having constant number of particles N and constant volume V, but the condition of constant energy E of the system is often impractical, as in most of the cases, the system exchanges energy with the surrounding environment at least. It is rather convenient to maintain constant temperature T of a system A by placing it in thermal contact with an appropriate heat reservoir B (Figure 1). In the present scenario where the exchange of energy is permitted, macrostate of the system is defined by some constant values of N, V and T.

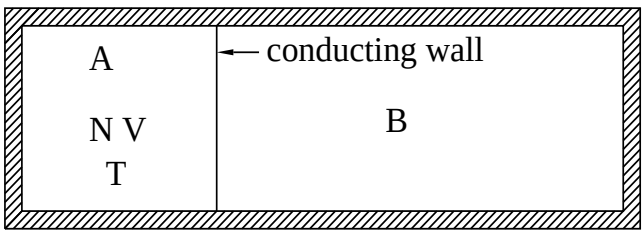

Figure 1: System of interest A is in thermal contact with the heat reservoir B so that temperature T of A remains constant through exchange of energy between A and B.

When we replace the elements of microcanonical ensemble having constant values of N, V and E by copies of the system having constant values for N, V and T, the ensemble is known as a canonical ensemble (Figure 2). Macrostate of the system is specified by N, V and T. In the canonical ensemble each element is in thermal contact with the heat reservoir. Obviously, in a canonical ensemble, energy E of the system

essentially varies such that its temperature T is kept constant. However, the total energy of the composite system comprising the system of interest and the reservoir has a constant value. The ensemble where elements are replaced by the composite system would obviously behave like a microcanonical ensemble, as the composite system has constant values for the number of particles, volume and energy.

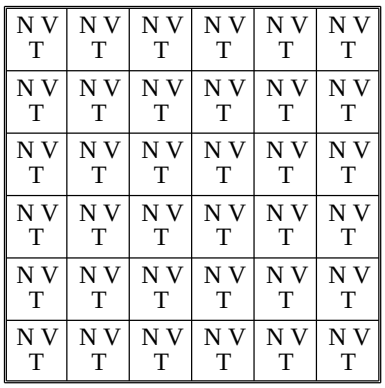

Figure 2: Canonical ensemble where each element has constant values of the number of particles N, volume V and temperature T.

In the present chapter, we shall discuss about a canonical ensemble where the elements are copies of the system of interest having constant values of N, V and T.

1. Canonical distribution

Let us consider an isolated system (Figure 1) comprising the system of interest A in thermal contact with the heat reservoir B. This composite system of A and B is a closed, isolated system characterized by constant values of N_0, V_0 and E_0. Suppose, N and N' are the number of particles, V and V' the volumes, and E and E' the energies of A and B, respectively. Then, we have

$$N + N' = N_0 = \text{constant}$$
$$V + V' = V_0 = \text{constant}$$
$$E + E' = E_0 = \text{constant}$$

As the reservoir B is supposed to be much larger than the system of interest A, we have

$$N << N' \qquad V << V' \qquad \text{and} \qquad E << E'$$

Since the composite system of A and B is considered as an isolated one, the microcanonical distribution, discussed in the preceding chapter, is applicable to the composite system. Then the probability $\mathrm{d}W$ that A and B are in the volume elements $\mathrm{d}\Gamma_1$ and $\mathrm{d}\Gamma_2$, respectively, of the phase space (Figure 3) is

$$\mathrm{d}W = C\ \delta\Big\{(E + E') - E_0\Big\}\ \mathrm{d}\Gamma_1\ \mathrm{d}\Gamma_2$$

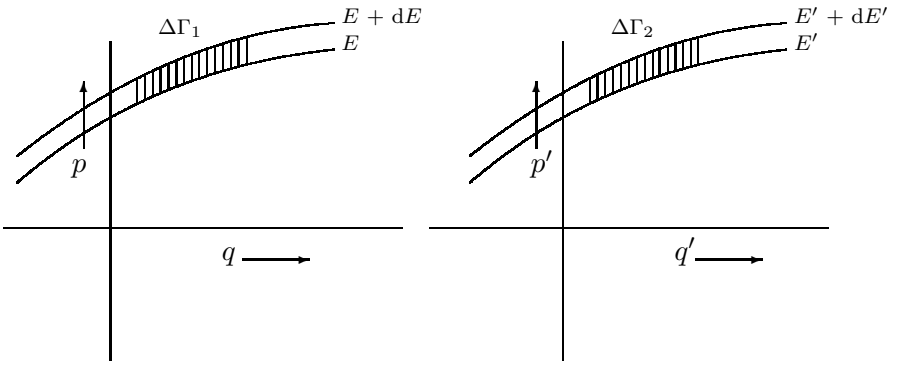

Figure 3: The system of interest A and the reservoir B are in the volume elements $\mathrm{d}\Gamma_1$ and $\mathrm{d}\Gamma_2$, respectively, of the phase space.

where δ is the Dirac-delta function, and C a constant. For the system A to exist in a definite quantum state with energy E_n, we have $E = E_n$, $\mathrm{d}\Gamma_1 = 1$, and the probability ρ_n to find the system A in this definite state is

$$\rho_n = \int \mathrm{d}W = \int C\delta(E_n + E' - E_0)\mathrm{d}\Gamma_2 = C\int \delta[E' - (E_0 - E_n)]\mathrm{d}\Gamma_2 \quad (4.1)$$

Now, the entropy $S_2(E')$ of the reservoir is

$$S_2(E') = k\ \ln(\Delta\Gamma_2)$$

Thus, we have

$$\Delta\Gamma_2 = \exp[S_2(E')/k]$$

The number of quantum states $\Gamma_2(E')$ of the reservoir are the functions of its energy E'. Then, we have

$$d\Gamma_2 = \frac{\partial\Gamma_2}{\partial E'}\ \mathrm{d}E' = \frac{\Delta\Gamma_2}{\Delta E'}\ \mathrm{d}E' = \frac{\exp[S_2(E')/k]}{\Delta E'}\ \mathrm{d}E' \quad (4.2)$$

Using equation (4.2) in (4.1), we get

$$\rho_n = C\int \delta[E' - (E_0 - E_n)]\ \frac{\exp[S_2(E')/k]}{\Delta E'}\ \mathrm{d}E'$$

By using the property of Dirac-delta function, we get

$$\rho_n = C\ \frac{\exp[S_2(E_0 - E_n)/k]}{\Delta(E_0 - E_n)} \tag{4.3}$$

The system A being small in comparison to the reservoir B, we have $E_n << E_0$ and thus, we get

$$\Delta(E_0 - E_n) = \Delta E_0 \tag{4.4}$$

Further, we can expand $S_2(E_0 - E_n)$ about E as

$$S_2(E_0 - E_n) = S_2(E_0) - \frac{\partial}{\partial E_0} S_2(E_0)\ E_n$$

where the higher order terms are neglected. For the temperature T of the reservoir B (as well as of the system A), we have

$$\frac{\partial}{\partial E_0} S_2(E_0) = \frac{1}{T}$$

and therefore,

$$S_2(E_0 - E_n) = S_2(E_0) - \frac{E_n}{T} \tag{4.5}$$

Using equations (4.4) and (4.5) in (4.3), we get

$$\rho_n = C\ \frac{\exp[S_2(E_0)/k]}{\Delta E_0}\ \exp(-E_n/kT) = D\ \exp(-E_n/kT) \tag{4.6}$$

where the normalization constant

$$D = C\ \exp\Big(S_2(E_0)/k\Big)\Big/\Delta E_0$$

is independent of the energy E_n of the system A. The normalization condition

$$\sum_n \rho_n = 1$$

gives

$$\sum_n D\ \exp(-E_n/kT) = 1$$

Thus, we have

$$\frac{1}{D} = \sum_n \exp(-E_n/kT) \tag{4.7}$$

Here, $D^{-1}(= Z_N)$ is known as the canonical partition function of the system A in quantum statistics. The Gibbs distribution function (equation 4.6) is

$$\rho_n = \frac{\exp(-E_n/kT)}{\sum_n \exp(-E_n/kT)} \tag{4.8}$$

This equations is known as the Gibbs canonical distribution or simply the canonical distribution for a closed system (in quantum statistics).

In classical statistics, expression for Gibbs distribution in phase space, similar to equation (4.6), is

$$\rho(q,p) = D\ \exp[-E(q,p)/kT] \tag{4.9}$$

where the energy $E(q,p)$ of the system is a function of the position and momentum coordinates. The normalization condition

$$\int \rho(q,p)\ \mathrm{d}q\ \mathrm{d}p = 1$$

gives

$$\int D\ \exp(-E(q,p)/kT)\ \mathrm{d}q\ \mathrm{d}p = 1$$

Thus, we have

$$\frac{1}{D} = \int \exp(-E(q,p)/kT)\ \mathrm{d}q\ \mathrm{d}p \tag{4.10}$$

Here, $D^{-1}(= Z_N)$ is known as the canonical partition function of the system A in classical statistics. The Gibbs distribution function in classical statistics is

$$\rho = \frac{\exp(-E(q,p)/kT)}{\int \exp(-E(q,p)/kT)\ \mathrm{d}q\ \mathrm{d}p}$$

1.1 Canonical average

Mean value of a physical quantity f using the Gibbs canonical distribution is

$$\langle f \rangle = \frac{\int f(q,p)\ \exp[-E(q,p)/kT]\ \mathrm{d}q\ \mathrm{d}p}{\int \exp[-E(q,p)/kT]\ \mathrm{d}q\ \mathrm{d}p} \qquad \text{(classical)}$$

and

$$\langle f \rangle = \frac{\sum_n f_n\ \exp(-E_n/kT)}{\sum_n \exp(-E_n/kT)} \qquad \text{(quantum)}$$

2. Canonical partition function

In canonical ensemble for a system of interest having some constant values of the number of particles N, volume V and temperature T, the partition function Z_N is

$$Z_N = \int \exp(-E(q,p)/kT)\ \mathrm{d}q\ \mathrm{d}p \qquad \text{(classical)} \tag{4.11}$$

and

$$Z_N = \sum_n \exp(-E_n/kT) \qquad \text{(quantum)}$$

In quantum statistics, the expression for the partition function is a dimensionless quantity. However, in the classical statistics, the expression is a dimensional quantity. In order to make it dimensionless, the volume element $\mathrm{d}q\ \mathrm{d}p$ is expressed in the corresponding number of quantum states by dividing it by h^{3N}, where N is the number of particles in the system of interest and h the Planck's constant. Thus, the partition function is

$$Z_N = \frac{1}{h^{3N}} \int \exp(-E(q,p)/kT)\ \mathrm{d}q\ \mathrm{d}p \tag{4.12}$$

Further, in accordance with the rule of correct Boltzmann counting, equation (4.12) is divided by $N!$. It helps in removing the Gibbs paradox. Hence, the partition function in classical statistics is finally modified to

$$Z_N = \frac{1}{N!h^{3N}} \int \exp\Big[-E(q,p)/kT\Big]\ \mathrm{d}q\ \mathrm{d}p \tag{4.13}$$

In most of the cases, the energy levels of a system are degenerate. Suppose, g_n is the degeneracy of a level having energy E_n. Thus, in quantum statistics, the partition function is

$$Z_N = \sum_n g_n\ \exp(-E_n/kT)$$

and the corresponding expression for the Gibbs distribution function is

$$\rho_n = \frac{g_n\ \exp(-E_n/kT)}{\sum_n g_n\ \exp(-E_n/kT)}$$

Thus, the probability of the system to find it in the level with energy E_n is directly proportional to the degeneracy (also called, the weight factor or statistical weight) of the level.

The canonical average of a physical quantity f using the Gibbs canonical distribution is now

$$\langle f \rangle = \frac{\sum_n g_n \ f_n \ \exp(-E_n/kT)}{\sum_n g_n \ \exp(-E_n/kT)}$$

Exercise 1. Show that the partition function Z of a system of N independent particles is equal to the product of the partition functions Z_i of individual particles. That is

$$Z = \prod_{i=1}^{N} Z_i \qquad \text{or} \qquad Z_1^N \qquad \text{when all particles are identical}$$

Solution: Let the space and momentum coordinates, and energy of N particles are, respectively, denoted by q_i, p_i and E_i, $i = 1, 2, \ldots, N$. The partition function of the system in three-dimensional space having energy $E = E_1 + E_2 + \ldots + E_N$ is

$$Z = \frac{1}{h^{3N}} \int \exp(-E/kT) \ \mathrm{d}q_1 \ \mathrm{d}q_2 \ldots \mathrm{d}q_N \ \mathrm{d}p_1 \ \mathrm{d}p_2 \ldots \mathrm{d}p_N$$

The partition function of first particle in three-dimensional space is

$$Z_1 = \frac{1}{h^3} \int \mathrm{e}^{-E_1/kT} \ \mathrm{d}q_1 \ \mathrm{d}p_1$$

The partition function of second particle in three-dimensional space is

$$Z_2 = \frac{1}{h^3} \int \mathrm{e}^{-E_2/kT} \ \mathrm{d}q_2 \ \mathrm{d}p_2$$

Similarly, we can calculate for all particles. The partition function of Nth particle in three-dimensional space is

$$Z_N = \frac{1}{h^3} \int \mathrm{e}^{-E_N/kT} \ \mathrm{d}q_N \ \mathrm{d}p_N$$

Thus, we have

$$Z_1 Z_2 \ldots Z_N = \frac{1}{h^{3N}} \int \mathrm{e}^{-(E_1+E_2+\ldots+E_N)/kT} \ \mathrm{d}q_1 \ \mathrm{d}q_2 \ldots \mathrm{d}q_N \ \mathrm{d}p_1 \ \mathrm{d}p_2 \ldots \mathrm{d}p_N$$

and therefore,

$$Z = Z_1 Z_2 \ldots Z_N = \prod_{i=1}^{N} Z_i$$

When all the particles are identical, we have $Z_1 = Z_2 = \ldots = Z_N$ and therefore, we have

$$Z = Z_1^N$$

Exercise 2. For a system of N oscillators, each of mass m and angular frequency ω, calculate the partition function (i) classically and (ii) quantum mechanically. Find internal energy, entropy and specific heat of the system.

Solution: (i) In the classical mechanics, the Hamiltonian of an oscillator is[1] $H = p^2/2m + m\omega^2 q^2/2$. Thus, the classical partition function for one-dimensional oscillator is[2]

$$Z_1 = \frac{1}{h}\int \mathrm{e}^{-E/kT}\ \mathrm{d}q\ \mathrm{d}p = \frac{1}{h}\int_{-\infty}^{\infty}\mathrm{e}^{-p^2/2mkT}\mathrm{d}p\ \int_{-\infty}^{\infty}\mathrm{e}^{-m\omega^2 q^2/2kT}\mathrm{d}q$$

$$= \frac{1}{h}\sqrt{2\pi mkT}\ \sqrt{\frac{2\pi kT}{m\omega^2}} = \frac{2\pi kT}{h\omega}$$

Since the partition function Z_N of a system of N independent particles is equal to the product of the partition function Z_1 of of individual particle, we have

$$Z_N = Z_1^N = \Big[\frac{2\pi kT}{h\omega}\Big]^N$$

The Helmholtz free energy F is

$$F = -kT\ \mathrm{ln}Z_N = -NkT\ \mathrm{ln}\Big[\frac{2\pi kT}{h\omega}\Big]$$

---

[1] We have

$$F = -kx \qquad x = A\ \sin(\omega t) \qquad \ddot{x} = -\omega^2 x$$

Therefore, we have

$$m\ \ddot{x} = -kx \qquad \ddot{x} = -(k/m)\ x \qquad \text{or} \qquad \omega^2 = (k/m)$$

Hence,

$$F = -m\omega^2 x = -\frac{\mathrm{d}V}{\mathrm{d}x}$$

The potential energy is

$$V = \frac{1}{2}\ m\omega^2 x^2$$

[2] Let $x = (ua)^{1/2}$ so that $\mathrm{d}x = a^{1/2}u^{-1/2}\ \mathrm{d}\ u/2$ and thus

$$\int_{-\infty}^{\infty}\exp(-x^2/a)\ \mathrm{d}x = 2\int_0^{\infty}\exp(-u)\ u^{-1/2}\ \mathrm{d}u = \sqrt{\pi a}$$

The entropy S is

$$S = -\frac{\partial F}{\partial T} = Nk\Big[1 + \ln\Big(\frac{2\pi kT}{\hbar\omega}\Big)\Big]$$

The internal energy U of the system is

$$U = F + ST = kNT$$

Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = Nk$$

showing that in classical statistics, the specific heat at constant volume does not depend on temperature.

(ii) In quantum mechanics, the energy of an oscillator is $E_n = (n + 1/2)\hbar\omega$. Thus, the quantum mechanical partition function is

$$Z_1 = \sum_n \mathrm{e}^{-E_n/kT} = \sum_{n=0}^{\infty} \mathrm{e}^{-(n+1/2)\hbar\omega/kT} = \mathrm{e}^{-\hbar\omega/2kT} \sum_{n=0}^{\infty} (\mathrm{e}^{-\hbar\omega/kT})^n$$
$$= \frac{\mathrm{e}^{-\hbar\omega/2kT}}{1 - \mathrm{e}^{-\hbar\omega/kT}} = \frac{1}{\mathrm{e}^{\hbar\omega/2kT} - \mathrm{e}^{-\hbar\omega/2kT}} = \frac{1}{2\ \sinh(\hbar\omega/2kT)}$$

Here, we have used the fact that $1 + x + x^2 + \ldots = (1 - x)^{-1}$. Since the partition function Z_N of a system of N independent particles is equal to the product of the partition function Z_1 of of individual particle, we have

$$Z_N = Z_1^N = \Big[2\ \sinh\Big(\frac{\hbar\omega}{2kT}\Big)\Big]^{-N}$$

The Helmholtz free energy F is

$$F = -kT\ \ln Z_N = NkT\ \ln\Big[2\ \sinh\Big(\frac{\hbar\omega}{2kT}\Big)\Big]$$

The entropy S is

$$S = -\frac{\partial F}{\partial T} = Nk\Big[\frac{\hbar\omega}{2kT}\ \coth\Big(\frac{\hbar\omega}{2kT}\Big) - \ln\Big\{2\ \sinh\Big(\frac{\hbar\omega}{2kT}\Big)\Big\}\Big]$$

The internal energy U of the system is

$$U = F + ST = \frac{N\hbar\omega}{2}\ \coth\Big(\frac{\hbar\omega}{2kT}\Big) = \frac{N\hbar\omega}{2}\Big[1 + \frac{2}{\mathrm{e}^{\hbar\omega/kT} - 1}\Big]$$

Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = \frac{Nk\ \mathrm{e}^{\hbar\omega/kT}}{(\mathrm{e}^{\hbar\omega/kT} - 1)^2}\Big[\frac{\hbar\omega}{kT}\Big]^2$$

It is obvious that when $(\hbar\omega/kT) \to 0$ the case (ii) converges into (i).

3. Maxwell distribution of velocities

In a gas, though the temperature T is constant, all the constituent particles do not move with one value of velocity. The particles rather show a distribution, called the Maxwell distribution, of velocities which can be derived in the following manner. Remembering the Gibbs distribution function, the probability that the system is in the volume element $\mathrm{d}q\ \mathrm{d}p$ is

$$\mathrm{d}W = A\ \exp[-E(q,p)/kT]\ \mathrm{d}q\ \mathrm{d}p \tag{4.14}$$

Energy of a particle is a sum of kinetic energy and potential energy

$$E(q,p) = \frac{p^2}{2m} + V(q) \tag{4.15}$$

where $V(q)$ is the potential energy and m the mass of each particle. Using equation (4.15) in (4.14), we get

$$\mathrm{d}W = A\ \exp\Big[-\frac{p^2}{2mkT}\Big]\ \exp\Big[-\frac{V}{kT}\Big]\ \mathrm{d}q\ \mathrm{d}p = \mathrm{d}W_p\ \mathrm{d}W_q$$

where $\mathrm{d}W_p$ and $\mathrm{d}W_q$ defined as

$$\mathrm{d}W_p = A_p\ \exp(-p^2/2mkT)\ \mathrm{d}p \tag{4.16}$$

$$\mathrm{d}W_q = A_q\ \exp(-V/kT)\ \mathrm{d}q$$

are the probability distributions for momentum and position coordinates, respectively. The constants A_p and A_q (such that $A = A_p\ A_q$) can be determined by the normalization conditions of $\mathrm{d}W_p$ and $\mathrm{d}W_q$ separately, so that

$$A_p \int \exp(-p^2/2mkT)\ \mathrm{d}p = 1 \qquad \text{and} \qquad A_q \int \exp[-V/kT]\ \mathrm{d}q = 1$$

We are interested only in the velocity distribution. In order to find the distribution of velocities, let us consider the probability distribution for the momentum coordinate of the particle. Using Cartesian components, we have

$$p^2 = p_x^2 + p_y^2 + p_z^2 \qquad \text{and} \qquad \mathrm{d}p = \mathrm{d}p_x\ \mathrm{d}p_y\ \mathrm{d}p_z \tag{4.17}$$

Using equation (4.17) in (4.16), we have the probability distribution

$$\mathrm{d}W_p = A_p\ \exp[-(p_x^2 + p_y^2 + p_z^2)/2mkT]\ \mathrm{d}p_x\ \mathrm{d}p_y\ \mathrm{d}p_z$$

The normalization condition gives

$$A_p \int_{-\infty}^{\infty} \exp[-(p_x^2 + p_y^2 + p_z^2)/2mkT] \; \mathrm{d}p_x \; \mathrm{d}p_y \; \mathrm{d}p_z = 1$$

$$A_p \int_{-\infty}^{\infty} \exp(-p_x^2/2mkT) \; \mathrm{d}p_x \int_{-\infty}^{\infty} \exp(-p_y^2/2mkT) \; \mathrm{d}p_y$$

$$\times \int_{-\infty}^{\infty} \exp(-p_z^2/2mkT) \; \mathrm{d}p_z = 1 \tag{4.18}$$

Hence,

$$A_p \; (2\pi mkT)^{3/2} = 1 \qquad \text{or} \qquad A_p = (2\pi mkT)^{-3/2} \tag{4.19}$$

Using equation (4.19) in (4.18), the probability distribution for momentum coordinates is

$$\mathrm{d}W_p = (2\pi mkT)^{-3/2} \exp[-(p_x^2 + p_y^2 + p_z^2)/2mkT] \mathrm{d}p_x \; \mathrm{d}p_y \; \mathrm{d}p_z \tag{4.20}$$

By converting the momentum components into the velocity components through the relations

$$p_x = m \; v_x \qquad p_y = m \; v_y \qquad p_z = m \; v_z$$

the probability distribution for velocity is

$$\mathrm{d}W_v = \Big(\frac{m}{2\pi kT}\Big)^{3/2} \exp[-m(v_x^2 + v_y^2 + v_z^2)/2kT] \; \mathrm{d}v_x \; \mathrm{d}v_y \; \mathrm{d}v_z \tag{4.21}$$

This is the Maxwell distribution for Cartesian components of velocity. This is the number of particles in the velocity ranges from v_x to $v_x + \mathrm{d}v_x$, from v_y to $v_y + \mathrm{d}v_y$, from v_z to $v_z + \mathrm{d}v_z$.

3.1 Maxwell distribution for absolute velocity

Maxwell distribution for absolute velocity can be derived in the following manner. If we use polar coordinates (v, θ, ϕ), where θ and ϕ are polar and azimuthal angles and v the absolute velocity

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

the polar coordinates (v, θ, ϕ) are related to the Cartesian coordinates (v_x, v_y, v_z) as

$$v_x = v \; \sin\theta \; \cos\phi \qquad v_y = v \; \sin\theta \; \sin\phi \qquad v_z = v \; \cos\theta$$

and the volume element is

$$\mathrm{d}v_x\ \mathrm{d}v_y\ \mathrm{d}v_z = v^2\ \mathrm{d}v\ \sin\theta\ \mathrm{d}\theta\ \mathrm{d}\phi$$

Hence, the probability distribution for velocity is

$$\mathrm{d}W_v = \Big(\frac{m}{2\pi kT}\Big)^{3/2}\exp\Big(-\frac{mv^2}{2kT}\Big)\ v^2\ \mathrm{d}v\ \sin\theta\ \mathrm{d}\theta\ \mathrm{d}\phi \tag{4.22}$$

Integrating (4.22) with respect to the angles θ and ϕ, we have

$$\mathrm{d}W_v = \Big(\frac{m}{2\pi kT}\Big)^{3/2}\exp\Big(-\frac{mv^2}{2kT}\Big)\ v^2\ \mathrm{d}v\int_0^{\pi}\sin\theta\ \mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi$$

$$= 4\pi\Big(\frac{m}{2\pi kT}\Big)^{3/2}\ \exp\Big(-\frac{mv^2}{2kT}\Big)\ v^2\ \mathrm{d}v = \rho_v\ \mathrm{d}v$$

Here, ρ_v is the probability density given by

$$\rho_v = 4\pi\Big(\frac{m}{2\pi kT}\Big)^{3/2}\exp\Big(-\frac{mv^2}{2kT}\Big)\ v^2 \tag{4.23}$$

and $\rho_v\ \mathrm{d}v$ gives the probability that velocity of a particle lies between v and $v + \mathrm{d}v$. It can be shown easily that

$$\int_0^{\infty}\rho_v\ \mathrm{d}v = 1$$

That is the probability density is normalized. Equation (4.23) shows that for small velocities we have

$$\rho_v = 4\pi\Big(\frac{m}{2\pi kT}\Big)^{3/2}v^2\ \Big[1 - \frac{mv^2}{2kT} + \frac{1}{2!}\Big(\frac{mv^2}{2kT}\Big)^2 - \ldots\Big] = 4\pi\Big(\frac{m}{2\pi kT}\Big)^{3/2}v^2$$

showing that when $v \to 0$, $\rho_v \to 0$. For high velocities, the exponential factor decreases much faster than the increase of v^2 factor and therefore, $\rho_v \to 0$. A trend of variation of $\rho_v/\sqrt{8m/\pi kT}$ versus $v/\sqrt{2kT/m}$ is shown in Figure 4.

3.2 Most probable velocity

The most probable value of velocity, v_{mp}, corresponding to the maximum value of ρ_v, can be obtained by considering the condition of maximum

$$\Big(\frac{\mathrm{d}\rho_v}{\mathrm{d}v}\Big)_{v=v_{mp}} = 0 \tag{4.24}$$

Using equation (4.23) in (4.24), we get

$$4\pi\Big(\frac{m}{2\pi kT}\Big)^{3/2}\,\Big[\exp\Big(-\frac{mv^2}{2kT}\Big)\Big(-\frac{mv}{kT}\Big)\,v^2+\exp\Big(-\frac{mv^2}{2kT}\Big)2v\Big]_{v=v_{mp}}=0$$

$$\Big[4\pi\Big(\frac{m}{2\pi kT}\Big)^{3/2}\,\exp\Big(-\frac{mv_{mp}^2}{2kT}\Big)\,v_{mp}\Big]\Big[-\frac{mv_{mp}^2}{kT}+2\Big]=0$$

Thus, we have

$$v_{mp}=\sqrt{\frac{2kT}{m}}$$

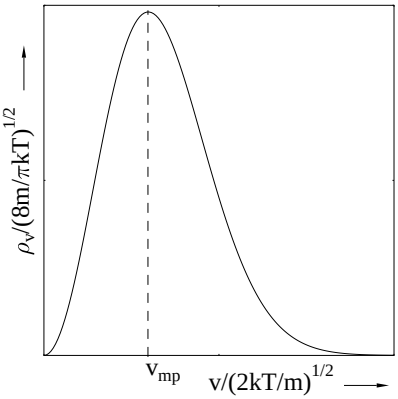

Figure 4: Maxwell distribution of velocities.

3.3 Mean kinetic energy

Mean value of kinetic energy of a particle, averaged over the Maxwell distribution, is

$$\langle E\rangle=\int_0^\infty\frac{1}{2}\,mv^2\rho_v\,\mathrm{d}v=2\pi m\Big(\frac{m}{2\pi kT}\Big)^{3/2}\int_0^\infty\exp\Big(-\frac{mv^2}{2kT}\Big)v^4\,\mathrm{d}v\quad(4.25)$$

For evaluation of the integral, let us put

$$\frac{mv^2}{2kT}=x\qquad\text{and}\qquad\frac{mv\,\mathrm{d}v}{kT}=\mathrm{d}x\qquad(4.26)$$

Using equation (4.26) in (4.25), we get

$$\langle E\rangle=\frac{2kT}{\pi^{1/2}}\int_0^\infty\mathrm{e}^{-x}x^{3/2}\,\mathrm{d}x=\frac{2kT}{\pi^{1/2}}\,\Gamma(5/2)=\frac{3}{2}\,kT$$

A particle has three degrees of freedom. So, the mean kinetic energy of a particle per degree of freedom is $kT/2$.

4. Thermodynamic quantities in a canonical ensemble

We know that entropy of a thermodynamical system is an explicit function of its energy, irrespective of whether the system is isolated or in thermal contact with some other systems. Thus, the entropy of a system of microcanonical ensemble with energy E is the same as that of the system of canonical ensemble with the mean energy E. Entropy S of a system is

$$S = k \ln(\Delta\Gamma) \tag{4.27}$$

where k is the Boltzmann constant and $\Delta\Gamma$ the statistical weight. The distribution function $\rho(E)$ is related to the statistical weight $\Delta\Gamma$ as

$$\rho(E)\ \Delta\Gamma = 1$$

Thus, we have

$$\Delta\Gamma = \frac{1}{\rho(E)} \tag{4.28}$$

From equation (4.8), Gibbs distribution function $\rho(E)$ is

$$\rho(E) = \frac{\exp(-E/kT)}{Z_N} \tag{4.29}$$

where Z_N is the canonical partition function. Equations (4.27), (4.28) and (4.29) can be rearranged as

$$S = k \ln[\exp(E/kT)Z_N] = \frac{E}{T} + k \ln(Z_N)$$

The internal energy U is E and the Helmholtz free energy F is

$$F = E - ST = -kT \ln Z_N \tag{4.30}$$

Since the free energy F depends on the macroscopic parameters whereas the partition function Z_N depends on the microscopic parameters, equation (4.30) provides a link between the macro-world and micro-world, and provides the basic relationship of statistical thermodynamics. For the known free energy, other thermodynamic properties of the system can be obtained in the following manner.

(i) Pressure P of the system is

$$P = -\frac{\partial F}{\partial V} = kT\ \frac{\partial}{\partial V}(\ln Z_N)$$

(ii) Entropy S of the system is

$$S = -\frac{\partial F}{\partial T} = k\ \frac{\partial}{\partial T}(T\ \ln Z_N)$$

(iii) Internal energy U is

$$U = F + ST = -kT\ \ln(Z_N) + kT\ \frac{\partial}{\partial T}(T\ \ln Z_N) = kT^2\ \frac{\partial}{\partial T}(\ln Z_N)$$

(iv) Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = 2kT\ \frac{\partial}{\partial T}(\ln Z_N) + kT^2\ \frac{\partial^2}{\partial T^2}(\ln Z_N)$$

Exercise 3. A system in thermal equilibrium has non-degenerate energies 0 and E at the temperature T. Calculate the thermodynamic properties of the system.

Solution: Let T be the temperature of the system. The partition function Z of the system is

$$Z = \mathrm{e}^{0/kT} + \mathrm{e}^{-E/kT} = 1 + \mathrm{e}^{-E/kT}$$

(i) Helmholtz free energy F of the system is

$$F = -kT\ \ln Z = -kT\ \ln\Big[1 + \mathrm{e}^{-E/kT}\Big]$$

(ii) Entropy S of the system is

$$S = -\frac{\partial F}{\partial T} = k\ \ln\Big[1 + \mathrm{e}^{-E/kT}\Big] + \frac{E}{T}\ \frac{1}{\mathrm{e}^{E/kT} + 1}$$

(iii) Internal energy U is

$$U = F + ST = \frac{E}{\mathrm{e}^{E/kT} + 1}$$

(iv) Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = k\Big(\frac{E}{kT}\Big)^2 \frac{\mathrm{e}^{E/kT}}{(\mathrm{e}^{E/kT} + 1)^2}$$

(a) At a low temperature $(E/kT) >> 1$ and 1 can be neglected in comparison to the exponential term, and we have

$$c_V = k\Big(\frac{E}{kT}\Big)^2 \mathrm{e}^{-E/kT}$$

Since with the decrease of T, the function $e^{-E/kT}$ reduces much faster than the increase of the function $(E/kT)^2$, therefore

$$c_V \to 0 \qquad \text{when} \qquad T \to 0$$

(b) At a high temperature $(E/kT) << 1$ and the exponential term can be expanded, and we have

$$c_V = \frac{k}{4}\Big(\frac{E}{kT}\Big)^2$$

Hence,

$$c_V \to 0 \qquad \text{when} \qquad T \to \infty$$

It shows that the specific heat at constant volume is zero at very large temperature and at zero Kelvin. In classical treatment the c_V does not depend on the temperature.

Exercise 4. A system in thermal equilibrium has non-degenerate energies 0, E, $2E$, ..., $(n-1)E$ at the temperature T. Calculate the thermodynamic properties of the system.

Solution: Let T be the temperature of the system. The partition function Z of the system is

$$Z = e^{0/kT} + e^{-E/kT} + e^{-2E/kT} \ldots e^{-(n-1)E/kT} = \frac{1 - e^{-nE/kT}}{1 - e^{-E/kT}}$$

(i) Helmholtz free energy F of the system is

$$F = -kT\ \ln Z = -kT\ \ln\Big[1 - e^{-nE/kT}\Big] + kT\ \ln\Big[1 - e^{-E/kT}\Big]$$

(ii) Entropy S of the system is

$$S = -\frac{\partial F}{\partial T} = k\ \ln\Big[1 - e^{-nE/kT}\Big] - \frac{nE}{T}\ \frac{1}{e^{nE/kT} - 1} - k\ \ln\Big[1 - e^{-E/kT}\Big]$$

$$+\frac{E}{T}\ \frac{1}{e^{E/kT} - 1}$$

(iii) Internal energy U is

$$U = F + ST = \frac{E}{e^{E/kT} - 1} - \frac{nE}{e^{nE/kT} - 1}$$

(iv) Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = k\Big(\frac{E}{kT}\Big)^2 \frac{e^{E/kT}}{(e^{E/kT} - 1)^2} - k\Big(\frac{nE}{kT}\Big)^2 \frac{e^{nE/kT}}{(e^{nE/kT} - 1)^2}$$

(a) At a low temperature $(E/kT) >> 1$ and 1 can be neglected in comparison to the exponential term, and we have

$$c_V = k\Big(\frac{E}{kT}\Big)^2 \mathrm{e}^{-E/kT} - k\Big(\frac{nE}{kT}\Big)^2 \mathrm{e}^{-nE/kT}$$

$$= k\Big(\frac{E}{kT}\Big)^2 \mathrm{e}^{-E/kT}\Big[1 - n^2 \mathrm{e}^{-(n-1)E/kT}\Big]$$

As n is large and T is small, the exponential term in the bracket can be neglected in comparison to 1 and we have

$$c_V = k\Big(\frac{E}{kT}\Big)^2 \mathrm{e}^{-E/kT}$$

Since with the decrease of T, the function $\mathrm{e}^{-E/kT}$ reduces much faster than the increase of the function $(E/kT)^2$, therefore

$$c_V \to 0 \qquad \text{when} \qquad T \to 0$$

(b) At a high temperature $(E/kT) << 1$ and the exponential term can be expanded, and we have

$$c_V = k\Big(\frac{E}{kT}\Big)^2 \frac{1}{(1 + (E/kT) \ldots - 1)^2} - k\Big(\frac{nE}{kT}\Big)^2 \frac{1}{(1 + (nE/kT) \ldots - 1)^2}$$

$$= k\Big(\frac{E}{kT}\Big)^2 \Big(\frac{kT}{E}\Big)^2 - k\Big(\frac{nE}{kT}\Big)^2 \Big(\frac{kT}{nE}\Big)^2 = 0$$

Thus, at high temperature also, the c_V is zero.

5. Classical system in a canonical ensemble

Consider a system comprising N identical structureless particles, each of mass m, enclosed in a volume V at temperature T. The total energy E of the system is

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(q) \tag{4.31}$$

where p_i's are the momentum coordinates of the particles, and $U(q)$ the potential of the system. Since the gas is specified by some constant values of N, V and T, it is a case of canonical ensemble. The dimensionless partition function in canonical ensemble is

$$Z_N = \frac{1}{h^{3N}} \int \exp(-E/kT)\ \mathrm{d}q\ \mathrm{d}p \tag{4.32}$$

Using equation (4.31) in (4.32), we get

$$Z_N = \frac{1}{h^{3N}} \int \exp\Big(- \sum_{i=1}^{3N} \frac{p_i^2}{2mkT} \Big) \exp\Big(- \frac{U}{kT} \Big) \, \mathrm{d}q \, \mathrm{d}p$$

$$= \frac{1}{h^{3N}} \int \exp\Big(- \sum_{i=1}^{3N} \frac{p_i^2}{2mkT} \Big) \, \mathrm{d}p \int \exp\Big(- \frac{U}{kT} \Big) \, \mathrm{d}q \tag{4.33}$$

Thus,

$$Z_N = \frac{I_N}{h^{3N}} \prod_{i=1}^{3N} \Big[\int \exp\Big(- \frac{p_i^2}{2mkT} \Big) \, \mathrm{d}p_i \Big] \tag{4.34}$$

where

$$I_N = \int \exp(-U/kT) \, \mathrm{d}q \tag{4.35}$$

is the configural integral of the system. We have

$$\int_{-\infty}^{\infty} \exp(-p_i^2/2mkT) \, \mathrm{d}p_i = \sqrt{2\pi mkT}$$

Using this value of the integral in equation (4.33), we have

$$Z_N = \frac{I_N}{h^{3N}} \, (2\pi mkT)^{3N/2} = \frac{I_N}{\lambda^{3N}}$$

where $\lambda = h/\sqrt{2\pi mkT}$ is the thermal wavelength. The thermal wavelength having dimension of length depends only on the kinetic temperature of the gas.

5.1 Case of an ideal gas

For an ideal gas, the constituent particles do not interact with one another and thus, the potential energy U of the gas is zero, and from equation (4.35) we have.

$$I_N = \int \mathrm{d}q_1 \, \ldots \, \mathrm{d}q_{3N} = V^N$$

as the integration over three coordinates of a particle contributes the volume V of the system. Thus, for an ideal gas, the partition function is

$$Z_N = \frac{V^N}{\lambda^{3N}}$$

(i) Free energy F of the system is

$$F = -kT \ln Z_N = -NkT \ln\Big(\frac{V}{\lambda^3}\Big)$$

Once the free energy of the system is known, we can calculate other thermodynamical quantities of the system.

(ii) Entropy S of the system is

$$S = -\Big(\frac{\partial F}{\partial T}\Big)_{N,V} = Nk \ln\Big(\frac{V}{\lambda^3}\Big) + \frac{3}{2}\, Nk \tag{4.36}$$

(iii) Internal energy U is

$$U = F + ST = \frac{3}{2}\, NkT$$

Average energy $\langle U\rangle$ per particle is

$$\langle U\rangle = \frac{U}{N} = \frac{3}{2}\, kT$$

A particle has three degree of freedom. So, the mean kinetic energy of a particle per degree of freedom is $kT/2$.

(iv) Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = \frac{3}{2}\, Nk$$

It shows that the specific heat at constant volume of a classical ideal gas is independent of temperature.

5.2 Gibbs paradox

In order to check the additive property of entropy of the gas in canonical ensemble, let us increase each of the volume V and number of particles N of the gas by a common factor p, then the entropy S' of the new system is

$$\begin{aligned} S' &= kpN \ln\Big(\frac{pV}{\lambda^3}\Big) + \frac{3}{2}\, pNk \\ &= p\Big[kN \ln\Big(\frac{V}{\lambda^3}\Big) + \frac{3}{2}\, Nk\Big] + pNk \ln(p) \end{aligned} \tag{4.37}$$

Using equation (4.36) in (4.37), we get

$$S' = pS + pNk \ln(p)$$

In the new system, particle density $(pN/pV) = N/V$ remains the same as in the old one. Following the additive property of entropy of the gas, the entropy of the new system should be pS. It shows that the entropy given by equation (4.36) does not satisfy the additive property. This is known as the Gibbs paradox.

5.3 Removal of Gibbs paradox

Gibbs paradox can be removed when we introduce a factor $N!$ empirically in the denominator of the partition function[3] so that it is

$$Z_N = \frac{1}{N!}\ \frac{V^N}{\lambda^{3N}} \tag{4.38}$$

Division by $N!$, we take into account for the fact that the particles are indistinguishable. Now, free energy F is

$$F = -kT\ \ln(Z_N) = -kT\ \ln\Big[\frac{1}{N!}\ \frac{V^N}{\lambda^{3N}}\Big]$$

Using Stirling formula, $\ln\ N! = N\ \ln(N) - N$, we have

$$F = -kTN - kTN\ \ln\Big[\frac{V}{N\lambda^3}\Big]$$

and the entropy S of the system, with the improved partition function, is

$$S = -\frac{\partial F}{\partial T} = kN\ \ln\Big[\frac{V}{N\lambda^3}\Big] + \frac{5}{2}\ Nk \tag{4.39}$$

Now, in order to check additive property of entropy of the gas, let us increase each of the volume V and number of particles N of the gas by a common factor p, then the entropy of the new system is

$$S' = kpN\ \ln\Big(\frac{pV}{pN}\ \frac{1}{\lambda^3}\Big) + \frac{5}{2}\ pNk = p\Big[\ln\Big(\frac{V}{N}\ \frac{1}{\lambda^3}\Big) + \frac{5}{2}\ Nk\Big] = pS$$

Thus, the entropy has the additive property. It shows that the entropy expressed by equation (4.39) is free from any imperfection which leads to the Gibbs paradox.

Exercise 5. Calculate thermodynamic quantities (A) classically and (B) quantum mechanically of a system comprising N non-interacting, identical, linear harmonic oscillators in thermal equilibrium.

Solution: Let us consider a system comprising N non-interacting, identical, linear harmonic oscillators, each of mass m, in thermal equilibrium at temperature T. Since the oscillators are in thermal equilibrium, it is the case of a canonical ensemble. The oscillators do not interact with one another and they are identical. Let us assume that each of the oscillators executes small oscillations with the same frequency ω. The situation can be dealt in two ways: (A) Classical treatment, and (B) Quantum mechanical treatment.

[3]This is known as the correction for the Boltzmann counting.

(A) Classical treatment

Total energy of the system of oscillators is

$$E(q,p) = \sum_{i=1}^{N} \Big[\frac{p_i^2}{2m} + \frac{1}{2}\, m\omega^2 q_i^2\Big] \tag{4.40}$$

where q_i and p_i are position and momentum coordinates of the i-th oscillator, respectively. The partition function of the system is

$$\begin{aligned} Z_N &= \frac{1}{h^N} \int \exp\Big(- \sum_{i=1}^{N} \Big[\frac{p_i^2}{2mkT} + \frac{m\omega^2 q_i^2}{2kT}\Big]\Big)\, \mathrm{d}q\ \mathrm{d}p \\ &= \frac{1}{h^N} \prod_{i=1}^{N} \Big[\int_{-\infty}^{\infty} \mathrm{e}^{-p_i^2/2mkT} \mathrm{d}p_i \int_{-\infty}^{\infty} \mathrm{e}^{-m\omega^2 q_i^2/2kT} \mathrm{d}q_i \Big] \end{aligned} \tag{4.41}$$

We have

$$\int_{-\infty}^{\infty} \exp(-p_i^2/2mkT)\ \mathrm{d}p_i = \sqrt{2\pi mkT} \tag{4.42}$$

and

$$\int_{-\infty}^{\infty} \exp(-m\omega^2 q_i^2/2kT)\ \mathrm{d}q_i = \sqrt{\frac{2\pi kT}{m\omega^2}} \tag{4.43}$$

Using equations (4.42) and (4.43) in (4.41), we get

$$Z_N = \frac{1}{h^N} \Big(2\pi mkT\Big)^{N/2} \Big(\frac{2\pi kT}{m\omega^2}\Big)^{N/2} = \Big(\frac{2\pi kT}{h\omega}\Big)^N$$

(i) The Helmholtz free energy F is

$$F = -kT\ \ln Z_N = -NkT\ \ln\Big[\frac{2\pi kT}{h\omega}\Big]$$

(ii) Entropy S of the system is

$$S = -\frac{\partial F}{\partial T} = Nk\ \ln\Big(\frac{2\pi kT}{h\omega}\Big) + Nk$$

(iii) Internal energy U is

$$U = F + ST = NkT$$

Thus, the mean energy per oscillator is kT.

(iv) Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = Nk$$

The specific heat at constant volume c_V is independent of the temperature. In case of the classical treatment, the c_V does not depends on the kinetic temperature.

(B) Quantum mechanical treatment

In quantum mechanics, energy of an oscillator is quantized and is expressed as

$$E_n = \hbar\omega\Big(n + \frac{1}{2}\Big)$$

where ω is the angular frequency and n can assume all possible integer values $n = 0, 1, 2, 3, \ldots$. The partition function of an oscillator is

$$Z_1 = \sum_{n=0}^{\infty} \exp(-E_n/kT) = \sum_{n=0}^{\infty} \exp[-\hbar\omega(n + 1/2)/kT]$$

$$= \exp(-\hbar\omega/2kT) + \exp(-3\hbar\omega/2kT) + \exp(-5\hbar\omega/2kT)$$

$$+\exp(-7\hbar\omega/2kT) + \ldots = \frac{\exp(-\hbar\omega/2kT)}{1 - \exp(-\hbar\omega/kT)}$$

As all the oscillators are identical, the partition function of the system is

$$Z_N = Z_1^N = \Big[\frac{\exp(-\hbar\omega/2kT)}{1 - \exp(-\hbar\omega/kT)}\Big]^N$$

(i) Free energy F of the system is

$$F = -kT\ \ln Z_N = -NkT\ \ln\Big[\frac{\exp(-\hbar\omega/2kT)}{1 - \exp(-\hbar\omega/kT)}\Big]$$

$$= \frac{N\hbar\omega}{2} + NkT\ \ln[1 - \exp(-\hbar\omega/kT)]$$

Once the free energy of the system is known, we can calculate other thermodynamical quantities of the system.

(ii) Entropy S of the system is

$$S = -\frac{\partial F}{\partial T} = -Nk\ \ln\Big[1 - \exp(-\hbar\omega/kT)\Big] + \frac{N\hbar\omega/T}{\exp(\hbar\omega/kT) - 1}$$

(iii) Internal energy U is

$$U = F + ST = \frac{N\hbar\omega}{2} + \frac{N\hbar\omega}{\exp(\hbar\omega/kT) - 1}$$

(iv) Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = Nk\Big(\frac{\hbar\omega}{kT}\Big)^2 \frac{\exp(\hbar\omega/kT)}{[\exp(\hbar\omega/kT) - 1]^2}$$

(a) At a low temperature, we have $(\hbar\omega/kT) >> 1$ and 1 can be neglected in comparison to the exponential term, and we have

$$c_V = Nk\Big(\frac{\hbar\omega}{kT}\Big)^2 \exp\Big(-\frac{\hbar\omega}{kT}\Big)$$

Since with the decrease of T, the function $e^{-\hbar\omega/kT}$ reduces much faster than the increase of the function $(\hbar\omega/kT)^2$, therefore

$$c_V \to 0 \qquad \text{when} \qquad T \to 0$$

(b) At a high temperature, we have $(\hbar\omega/kT) << 1$ and the exponential term can be expanded, and we have

$$c_V = Nk\Big(\frac{\hbar\omega}{kT}\Big)^2 \frac{1 + \hbar\omega/kT + \ldots}{(1 + \hbar\omega/kT + \ldots - 1)^2}$$

It gives

$$c_V \to Nk \qquad \text{when} \qquad T \to \infty$$

It shows that the classical result for c_V is valid at high temperature.

Exercise 6. In a system of N independent particles, each particle can have only one of the two energies, $-\epsilon$ and ϵ. Find the thermodynamic weight W_i of a state with the total energy $E = M\epsilon$, where M can have the values from $-N$ to N in the steps of unity. Find out thermodynamic quantities of the system for $E < 0$.

Solution: Suppose N_1 particles are in the state with energy $-\epsilon$ and N_2 in the state with energy ϵ, total energy of the system is

$$E = M\epsilon = -N_1\epsilon + N_2\epsilon$$

so that $M = N_2 - N_1$. Since $N = N_2 + N_1$, we have

$$N_1 = \frac{1}{2}(N - M) \qquad N_2 = \frac{1}{2}(N + M)$$

There are $N!/(N_1!\ N_2!)$ possible ways of choosing N_1 particles out of N to occupy the state $-\epsilon$ and each of them gives a different microscopic state with energy E. Hence the thermodynamic weight is

$$W_i = \frac{N!}{[\frac{1}{2}(N - M)]!\ [\frac{1}{2}(N + M)]!}$$

The entropy of the system is

$$S = k\ \ln W_i k\ \ln\Big[\frac{N!}{[\frac{1}{2}(N - M)]!\ [\frac{1}{2}(N + M)]!}\Big]$$

On applying the Stirling formula, we get

$$S = -k[N_1 \ln(N_1/N) + N_2 \ln(N_2/N)]$$

Here, we used Stirling formula. The temperature T is

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial M}\,\frac{\partial M}{\partial E} = \frac{1}{\epsilon}\,\frac{\partial S}{\partial M} = \frac{k}{2\epsilon}\ln\left(\frac{N-M}{N+M}\right)$$

This equation shows that $T < 0$ for $M > 0$ ($E > 0$). This case is unacceptable on the physical ground. However, the system is normal in the range $M < 0$ ($E < 0$) and we can discuss the properties of this system for this case. From this equation, we have

$$\frac{N_1}{N_2} = \frac{N-M}{N+M} = \exp(2\epsilon/kT)$$

Therefore,

$$\frac{N_1}{N} = \frac{\exp(\epsilon/kT)}{\exp(\epsilon/kT) + \exp(-\epsilon/kT)}$$

and

$$\frac{N_2}{N} = \frac{\exp(-\epsilon/kT)}{\exp(\epsilon/kT) + \exp(-\epsilon/kT)}$$

These relations give the probabilities of finding any one particle in the states $-\epsilon$ and ϵ, respectively. The energy

$$E = N_2\epsilon - N_1\epsilon = -N\epsilon\,\tanh(\epsilon/kT)$$

The specific heat at constant volume c_V is

$$c_V = \frac{\partial E}{\partial T} = Nk(\epsilon/kT)^2\,\mathrm{sech}^2(\epsilon/kT)$$

Exercise 7. Suppose a system comprising N identical particles is placed in a uniform magnetic field H and is kept at a temperature T. When a particle having spin 1/2 is placed in a magnetic field H, its each energy level splits into two with changes in energies by $-\mu H$ and μH and the particle has a magnetic moment μ or $-\mu$ along the direction of the magnetic field, respectively. Find expressions for internal energy, entropy, specific heat and total magnetic moment M of this system with the help of the canonical distribution.

Solution: As the spins of particles are independent of each other, the partition function of the total system Z_N is equal to the product of

the partition functions for spins of individual particle. The partition function for spins of individual particle is

$$Z_1 = \mathrm{e}^{\mu H/kT} + \mathrm{e}^{-\mu H/kT} = 2\ \cosh(\mu H/kT)$$

As the particles are identical, the partition function of the system is

$$Z_N = Z_1^N = [2\ \cosh(\mu H/kT)]^N$$

(i) The Helmholtz free energy is

$$F = -kT\ \ln Z_N = -NkT\ \ln[2\ \cosh(\mu H/kT)]$$

(ii) The entropy is

$$S = -\frac{\partial F}{\partial T} = Nk\ [\ln\{2\ \cosh(\mu H/kT)\} - (\mu H/kT)\ \tanh(\mu H/kT)]$$

(iii) Total energy is

$$U = F + TS = -N\mu H\ \tanh(\mu H/kT)$$

(iv) Total magnetic moment is

$$M = -\frac{\partial F}{\partial H} = N\mu\ \tanh(\mu H/kT)$$

(v) The specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = Nk\ (\mu H/kT)^2\ \mathrm{sech}^2(\mu H/kT)$$

The c_V depends on the temperature also.

Exercise 8. For a system of N identical oscillators, each with a characteristic frequency ω, obtain the partition function Z_N of the system and calculate the number of states $W(E)$ for a given total energy.

Solution: As the particles are independent of each other, the partition function of the total system Z_N is equal to the product of the partition functions for individual particle. For a single harmonic oscillator with energy $E_n = (n + 1/2)\hbar\omega$, the partition function is

$$Z_1 = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta E_n} = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta(n+1/2)\hbar\omega}$$

$$= \mathrm{e}^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \mathrm{e}^{-n\beta\hbar\omega} = \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1 - \mathrm{e}^{-\beta\hbar\omega}}$$

Thus, the partition function for a system of N oscillators is[4]

$$Z_N = Z_1^N = \mathrm{e}^{-N\beta\hbar\omega/2}(1 - \mathrm{e}^{-\beta\hbar\omega})^{-N}$$

$$= \mathrm{e}^{-N\beta\hbar\omega/2} \sum_{i=0}^{\infty} {}^{-N}C_i \ (-1)^i \ \mathrm{e}^{-i\beta\hbar\omega}$$

$$= \sum_{i=0}^{\infty} \frac{(N+i-1)!}{(N-1)!i!} \ \mathrm{e}^{-(i+N/2)\beta\hbar\omega}$$

This relation shows that there are $W = (N+i-1)!/(N-1)!i!$ states for each discrete energy level $E = (i + N/2)\hbar\omega$ ($i = 0, 1, 2, \ldots$).

Exercise 9. Consider a system of N particles, each of mass m, enclosed in an infinitely long cylindrical container placed in a uniform gravitational field. The system is in thermal equilibrium. Obtain expressions for the classical partition function, Helmholtz free energy, entropy, internal energy and specific heat of the system.

Solution: Let us take consider a cylinder whose axis is along the z-axis of the Cartesian coordinate system and base is in the plane $z = 0$. Suppose there are N identical particles in a system. Each of the particles is moving independently and there is no potential energy. Total energy of a particle is

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + mgz$$

Thus, the partition function of a single particle is

$$Z_1 = \frac{1}{h^3} \int \mathrm{e}^{-E/kT} \ \mathrm{d}x \ \mathrm{d}y \ \mathrm{d}z \ \mathrm{d}p_x \ \mathrm{d}p_y \ \mathrm{d}p_z$$

$$= \frac{1}{h^3} \int \mathrm{e}^{-(p_x^2+p_y^2+p_z^2)/2mkT} \mathrm{e}^{-mgz/kT} \ \mathrm{d}x \ \mathrm{d}y \ \mathrm{d}z \ \mathrm{d}p_x \ \mathrm{d}p_y \ \mathrm{d}p_z$$

[4] We have

$${}^{-N}C_i \ (-1)^i = (-1)^i \ \frac{(-N)(-N-1)(-N-2)\ldots(-N-i+1)}{i!}$$

$$= \frac{(N)(N+1)(N+2)\ldots(N+i-1)}{i!} = \frac{(N+i-1)!}{(N-1)!i!}$$

$$= \frac{\sigma}{h^3}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\int_0^\infty \mathrm{e}^{-mgz/kT}\,\mathrm{d}z = \frac{\sigma kT}{mg}(2\pi mkT)^{3/2}$$

where σ is cross section of the container. As the particles are independent of each other, the partition function of the total system Z_N is equal to the product of the partition functions for individual particle. Thus, we have

$$Z_N = \frac{1}{N!}(Z_1)^N = \frac{1}{N!}\left(\frac{\sigma kT}{mg}\right)^N\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}$$

where a factor $N!$ is introduced for removing the Gibbs paradox.

(i) The Helmholtz free energy F of the system is

$$F = -kT\,\ln(Z_N) = -NkT\,\ln\left[\frac{\sigma kTe}{Nmg}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\right]$$

(ii) The entropy S of the system is

$$S = -\frac{\partial F}{\partial T} = Nk\,\ln\left[\frac{\sigma kTe}{Nmg}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\right] + \frac{5}{2}\,NkT$$

(iii) The internal energy U is

$$U = F + ST = \frac{5}{2}\,NkT$$

(iv) The specific heat c_V is

$$c_V = \frac{\partial U}{\partial T} = \frac{5}{2}\,Nk$$

This specific heat is larger than the specific heat $c_V = 3Nk/2$ of an ideal gas at constant volume, because with the increase of temperature, molecules rise and increase the potential energy.

6. Equivalence of microcanonical and canonical ensembles

In a microcanonical ensemble, the energy of the system remains almost fixed. On the other hand in the canonical system, in order to maintain thermal equilibrium, the energy E of the system of interest does not remains constant, but it varies. However, the thermodynamical quantities of a system derived through these two approaches are identical showing

that these two approaches are consistent. The reason for this equivalence between these two approaches can be understood in the following manner. In the canonical ensemble, the mean energy $\langle E \rangle$ is

$$U = \langle E \rangle = \frac{\sum_n E_n \; g_n \; \exp(-\beta E_n)}{\sum_n g_n \; \exp(-\beta E_n)} \tag{4.44}$$

where $\beta = 1/kT$. Differentiating equation (4.44) with respect to β, we get

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_n E_n^2 \; g_n \; \exp(-\beta E_n)}{\sum_n g_n \; \exp(-\beta E_n)} + \Big[\frac{\sum_n E_n g_n \; \exp(-\beta E_n)}{\sum_n g_n \; \exp(-\beta E_n)}\Big]^2$$

$$= -\langle E^2 \rangle + \langle E \rangle^2$$

The mean square fluctuation of energy is

$$\langle (\Delta E)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial U}{\partial \beta} = kT^2 \; \frac{\partial U}{\partial T} = kT^2 c_V$$

where c_V is the specific heat at constant volume. The relative root mean square fluctuation of energy E is given as

$$\frac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle E \rangle} = \frac{\sqrt{kT^2 c_V}}{U}$$

which is of the order of $O(N^{-1/2})$, where N is the number of particles in the system. As the number of particles N in a system is large, the relative mean square fluctuation in E is negligible. After neglecting the fluctuation of E, a system in the canonical ensemble has an energy almost equal to the mean energy U. Hence, the canonical ensemble for a system is equivalent to the microcanonical ensemble for the same system and the results obtained by them are practically identical.

7. Problems and questions

1. Which of the three physical parameters remain constant in the system of interest in canonical ensemble

   N, V, E, T, μ

   Ans. N, V, T

2. Derive an expression for canonical distribution and canonical partition function of a system in quantum statistics as well as in classical statistics.

3. For a system of N oscillators, each of mass m and angular frequency ω, calculate the partition function (i) classically and (ii) quantum mechanically. Show that for the classical case, the specific heat does not depend on temperature whereas it does depend on temperature in the quantum mechanical case. .

4. Derive an expression for Maxwell distribution of velocities. Show that

   (i) the most probable velocity of a particle is $\sqrt{2kT/m}$

   (ii) the mean kinetic energy of a particle per degree of freedom is $kT/2$.

5. Derive an expression for mean kinetic energy of a particle in the Maxwell distribution.

6. Derive expressions for physical quantities for an ideal gas in canonical ensemble.

7. Show that mean kinetic energy of a particle per degree of freedom is $kT/2$.

8. What is Gibbs paradox in canonical ensemble? How it is rectified.

9. Calculate thermodynamic quantities of a system comprising non-interacting, identical, linear harmonic oscillators in thermal equilibrium.

10. Calculate partition function for a classical system in canonical ensemble.

11. Derive an expression for entropy of an ideal gas in canonical ensemble. Check if it is free from Gibbs paradox. If not, how to remove the paradox.

12. Write notes on the following

    (i) Canonical distribution

    (ii) Canonical partition function

    (iii) Gibbs paradox in canonical ensemble

V. Grand Canonical Ensemble

In the previous chapter, we discussed about a canonical ensemble, where the volume V, number of particles N and temperature T of the system of interest had constant values. Hence, the exchange of energy of the system was permitted so that the temperature was kept constant. Variation of the number of particles of the system was however not allowed. There are a number of physical as well as chemical systems which do not support the concept of a constant number of particles. Such a system either exchanges particles with the others or generates/annihilates a number of particles of a definite type. A simple example of such system is a container having electromagnetic radiation (a gas of photons). The number of photons in the container does not remain constant as they are being continuously emitted as well as absorbed by the walls of the container. Such a system where variation of both the energy E and the number of particles N is allowed cannot be treated under microcanonical or canonical ensemble, discussed in the preceding chapters.

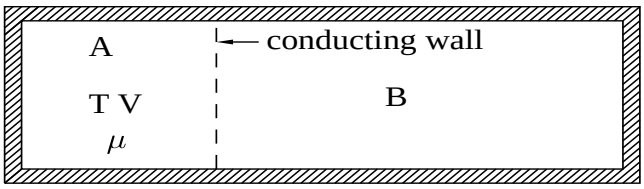

Figure 1: The system of interest A is in contact with the reservoir B so that exchange of energy and particles between them is feasible. For the system A, the volume V, temperature T, and chemical potential μ have constant values.

We consider a system, in which variation of its energy and number of particles is permitted, is in the contact with a reservoir with whom the exchange of energy as well as particles is feasible. Now, for the system of interest, placed in contact with the reservoir (Figure 1), the volume V, temperature T and chemical potential[1] μ have constant values.

When we replace the elements of a microcanonical ensemble having

[1] About the chemical potential μ we shall discuss after a while.

constant values of N, V and E by the copies of a system having constant values of V, T and μ, the ensemble is known as the grand canonical ensemble (Figure 2). In the grand canonical ensemble, each element is in contact with the reservoir where exchange of energy and particles is feasible. Obviously, in a grand canonical ensemble, energy E and the number of particles N of the system vary. However, the composite system comprising the system of interest and the reservoir has constant values of energy and therefore, the ensemble of the composite system behaves like a microcanonical ensemble.

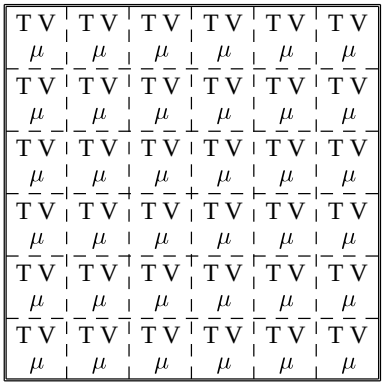

Figure 2: Grand canonical ensemble where each element has constant values of volume V, temperature T and chemical potential μ.

In the present chapter, we shall discuss about the grand canonical ensemble where the elements are the copies of the system of interest having constant values of volume V, temperature T and chemical potential μ. Values of chemical potential μ for some molecules in the gas phase at pressure $P = 1$ atm and temperature $T = 298$ K are given in the following table.

Molecule	μ (k cal/mol)
H_2	0.00
HI	0.31
I_2	4.63
N_2	0.00
NO_2	12.39
NH_3	−3.98
N_2O_4	23.49

1. Grand canonical distribution

Let us consider a system of interest A in contact with a reservoir B (Figure 1) with whom it may exchange energy as well as particles. The system of interest has constant values of volume V, temperature T and chemical potential μ. Let N and N' be the number of particles, and E and E' the energies of the system and reservoir, respectively. There may be exchange of energy as well as particles between the two. However, the total energy E_0 of the composite system is constant and we have

$$E + E' = E_0$$

As the reservoir (B) is supposed to be much larger than the system of interest (A), we have $E << E'$. Since the composite system of A and B is considered as an isolated one and total energy does not change, the microcanonical distribution, discussed earlier, is applicable to the composite system. Then the probability $\mathrm{d}W$ that A and B are in the volume elements $d\Gamma_1$ and $d\Gamma_2$, respectively, of the phase space (Figure 3) is

$$\mathrm{d}W = C\delta(E + E' - E_0)\ \mathrm{d}\Gamma_1\ \mathrm{d}\Gamma_2$$

where δ is the Dirac-delta function, and C a constant. For the system A to exist in a definite quantum state with energy E_{nN}, we have $E = E_{nN}$, $d\Gamma_1 = 1$, and the probability ρ_{nN} to find the system A in this definite state is

$$\rho_{nN} = \int \mathrm{d}W = \int C\delta(E_{nN} + E' - E_0)\mathrm{d}\Gamma_2$$

$$= C\int \delta[E' - (E_0 - E_{nN})]\mathrm{d}\Gamma_2 \tag{5.1}$$

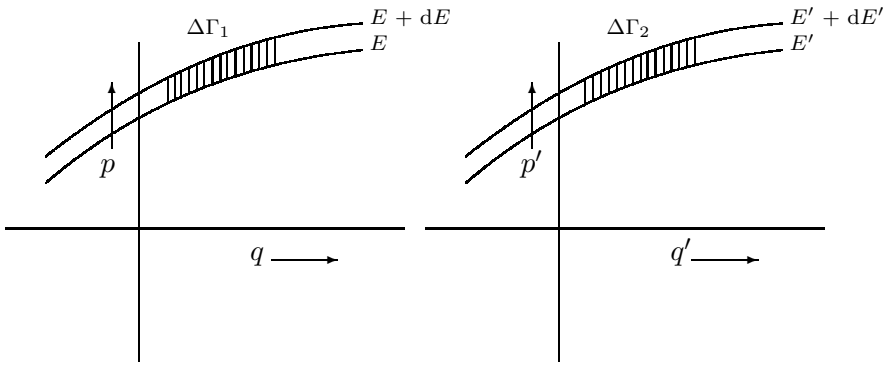

Figure 3: System of interest A and the reservoir B are in the volume elements $d\Gamma_1$ and $d\Gamma_2$, respectively, of the phase space.

The entropy $S_2(E', N')$ of the reservoir is

$$S_2(E', N') = k \ln(\Delta\Gamma_2) \qquad \text{Thus,} \qquad \Delta\Gamma_2 = \exp\Big[\frac{S_2(E', N')}{k}\Big]$$

The number of quantum states $\Gamma_2(E', N')$ of the reservoir are the functions of its energy E' and number of particles N'. For a given number N' of particles, we have

$$d\Gamma_2 = \frac{\partial\Gamma_2}{\partial E'}\,\mathrm{d}E' = \frac{\Delta\Gamma_2}{\Delta E'}\,\mathrm{d}E' = \frac{\exp[S_2(E', N')/k]}{\Delta E'}\,\mathrm{d}E' \tag{5.2}$$

Using equation (5.2) in (5.1), we get

$$\rho_{nN} = C \int \delta[E' - (E_0 - E_{nN})]\,\frac{\exp[S_2(E', N')/k]}{\Delta E'}\,\mathrm{d}E'$$

By using the property of Dirac-delta function, we get

$$\rho_{nN} = C\,\frac{\exp[S_2(E_0 - E_{nN}, N')/k]}{\Delta(E_0 - E_{nN})}$$

$$= C\,\frac{\exp[S_2(E_0 - E_{nN}, N_0 - N)/k]}{\Delta(E_0 - E_{nN})} \tag{5.3}$$

Here, N_0 is taken as the total number of particles at some instant. The system A being small in comparison to the reservoir B, we have $E_{nN} << E_0$ and thus, we have

$$\Delta(E_0 - E_{nN}) = \Delta E_0 \tag{5.4}$$

Further, we can expand $S_2(E_0 - E_{nN}, N_0 - N)$ as

$$S_2(E_0 - E_{nN}, N_0 - N) = S_2(E_0, N_0) - \Big[\frac{\partial}{\partial E_0} S_2(E_0, N_0)\Big]_{N_0} E_{nN} - \Big[\frac{\partial}{\partial N_0} S_2(E_0, N_0)\Big]_{E_0} N$$

For temperature T of the reservoir B (as well as of the system A), we have

$$\frac{\partial}{\partial E_0} S_2(E_0, N_0) = \frac{1}{T} \qquad \text{and} \qquad \frac{\partial}{\partial N_0} S_2(E_0, N_0) = -\frac{\mu}{T}$$

and therefore, we have

$$S_2(E_0 - E_{nN}, N_0 - N) = S_2(E_0, N_0) - \frac{E_{nN}}{T} + \frac{\mu N}{T} \tag{5.5}$$

Using equations (5.4) and (5.5) in (5.3), we get

$$\rho_{nN} = C\ \frac{\exp[S_2(E_0, N_0)/k]}{\Delta E_0}\ \exp\Big[-\frac{(E_{nN} - \mu N)}{kT}\Big]$$

$$= D\ \exp\Big[\frac{(\mu N - E_{nN})}{kT}\Big] \tag{5.6}$$

where the normalization constant

$$D = C\ \frac{\exp[S_2(E_0, N_0)/k]}{\Delta E_0}$$

is independent of the energy E_{nN} and number of particles N of the system A. The normalization condition

$$\sum_n \sum_N \rho_{nN} = 1$$

gives

$$\sum_n \sum_N D\ \exp\Big[\frac{\mu N - E_{nN}}{kT}\Big] = 1$$

Thus, we have

$$\frac{1}{D} = \sum_n \sum_N \exp\Big[\frac{\mu N - E_{nN}}{kT}\Big]$$

Here, $D^{-1}(= Z_\mu)$ is known as the grand canonical partition function of the system A in quantum statistics. The Gibbs distribution function (equation 5.6) in quantum statistics is

$$\rho_{nN} = \frac{\exp\Big[(\mu N - E_{nN})\Big/kT\Big]}{\sum_n \sum_N \exp\Big[(\mu N - E_{nN})\Big/kT\Big]}$$

This equations is known as the Gibbs grand canonical distribution or simply the grand canonical distribution for a closed system.

In the classical statistics, expression for Gibbs distribution in phase space, similar to equation (5.6), is

$$\rho_N(q, p) = D\ \exp\Big[\frac{\mu N - E_N(q, p)}{kT}\Big]$$

where the energy $E_N(q, p)$ of the system is a function of the position and momentum coordinates. The normalization condition

$$\sum_N \int \rho_N(q, p)\ \mathrm{d}q\ \mathrm{d}p = 1$$

gives

$$\sum_N \int D\, \exp\Big[\frac{\mu N - E_N(q,p)}{kT}\Big]\, \mathrm{d}q\, \mathrm{d}p = 1$$

$$\sum_N D\, \exp\Big(\frac{\mu N}{kT}\Big)\Big\{\int \exp\Big[-\frac{E_N(q,p)}{kT}\Big]\, \mathrm{d}q\, \mathrm{d}p\Big\} = 1$$

Thus,

$$\frac{1}{D} = \sum_N \exp\Big(\frac{\mu N}{kT}\Big)\Big\{\int \exp\Big[-\frac{E_N(q,p)}{kT}\Big]\, \mathrm{d}q\, \mathrm{d}p\Big\}$$

Here, $D^{-1}(= Z_\mu)$ is known as the grand canonical partition function of the system A in classical statistics. This partition function is a dimensional quantity. In order to make it dimensionless, it is divided by h^{3N}. Thus, the partition function in classical statistics is

$$Z_\mu = \sum_N \frac{1}{h^{3N}}\Big\{\exp\Big(\frac{\mu N}{kT}\Big)\int \exp\Big[-\frac{E_N(q,p)}{kT}\Big]\, \mathrm{d}q\, \mathrm{d}p\Big\}$$

The Gibbs distribution function in classical statistics is

$$\rho_N = \frac{\exp\Big(\Big\{\mu N - E_N(q,p)\Big\}\Big/kT\Big)}{Z_\mu}$$

1.1 Grand canonical average

Mean value of a physical quantity f using the Gibbs grand canonical distribution is

$$\langle f\rangle = \frac{\sum_N\{\int f_N\, \exp[\{\mu N - E_N(q,p)\}/kT]\, \mathrm{d}q\, \mathrm{d}p\}}{\sum_N\{\exp(\mu N/kT)\int \exp[-E_N(q,p)/kT]\, \mathrm{d}q\, \mathrm{d}p\}} \qquad \text{(classical)}$$

$$\langle f\rangle = \frac{\sum_N \sum_n f_{nN}\, \exp[(\mu N - E_{nN})/kT]}{\sum_N \sum_n \exp[(\mu N - E_{nN})/kT]} \qquad \text{(quantum)}$$

2. Grand canonical partition function

In a grand canonical ensemble for the system of interest having constant values of volume V, temperature T and chemical potential μ, the partition function Z_μ is

$$Z_\mu = \sum_N \frac{1}{h^{3N}}\Big\{\exp\Big(\frac{\mu N}{kT}\Big)\int \exp\Big[-\frac{E_N(q,p)}{kT}\Big]\, \mathrm{d}q\, \mathrm{d}p\Big\} \quad \text{(classical)} \quad (5.7)$$

and

$$Z_\mu = \sum_n \sum_N \exp\Big[\frac{\mu N - E_{nN}}{kT}\Big] \qquad \text{(quantum)}$$

In quantum statistics, the expression for partition function is a dimensionless quantity. However, in the classical statistics, the expression is a dimensional quantity. In order to make it dimensionless the volume element $\mathrm{d}q\ \mathrm{d}p$ is expressed in the corresponding number of quantum states by dividing it by h^{3N}, where N is the number of particles in the system of interest and h the Planck's constant. Thus, the partition function is

$$Z_\mu = \sum_N \frac{1}{h^{3N}} \Big\{ \exp\Big(\frac{\mu N}{kT}\Big) \int \exp\Big[- \frac{E_N(q,p)}{kT}\Big]\ \mathrm{d}q\ \mathrm{d}p \Big\}$$

Further, in accordance with the rule of correct Boltzmann counting, equation (5.7) is divided by $N!$. It helps in removing the Gibbs paradox. Hence, the partition function in classical statistics is finally modified to

$$Z_\mu = \sum_N \frac{1}{N! h^{3N}} \Big\{ \exp\Big(\frac{\mu N}{kT}\Big) \int \exp\Big[- \frac{E_N(q,p)}{kT}\Big]\ \mathrm{d}q\ \mathrm{d}p \Big\} \qquad (5.8)$$

In quantum statistics, the Gibbs distribution function is

$$\rho_{nN} = \frac{\exp[(\mu N - E_{nN})/kT}{Z_\mu} \qquad (5.9)$$

In most of the cases, the energy levels of a system are degenerate. Suppose, g_n is the degeneracy of the level having energy E_{nN}. Thus, in quantum statistics, the partition function is

$$Z_\mu = \sum_n \sum_N g_n\ \exp\Big[\frac{\mu N - E_{nN}}{kT}\Big]$$

and the corresponding expression for the Gibbs distribution function is

$$\rho_{nN} = \frac{g_n\ \exp[(\mu N - E_{nN})\Big/ kT]}{\sum_n \sum_N g_n\ \exp[(\mu N - E_{nN})\Big/ kT]}$$

Thus, the probability of the system to find it in the level with energy E_{nN} is directly proportional to the degeneracy (also called, the weight factor or statistical weight) of the level.

3. Thermodynamic quantities in a grand canonical ensemble

In a microcanonical as well as canonical ensemble, the number of particles in the system of interest had constant values and the entropy was a function of energy only. In the present case, the number of particles in the system does not have constant value, and therefore the entropy is a function of energy as well as the number of particles both. The entropy of a system of the grand canonical ensemble with mean energy E and mean number of particles N will be equal to the entropy of the system in a microcanonical ensemble with energy E and number of particles N. The entropy S of a system is

$$S = k\ \ln(\Delta\Gamma) \tag{5.10}$$

where k is the Boltzmann constant and $\Delta\Gamma$ the statistical weight. The distribution function $\rho(E, N)$ is related to the statistical weight $\Delta\Gamma$ as

$$\rho(E, N)\ \Delta\Gamma = 1 \qquad \text{and thus,} \qquad \Delta\Gamma = \frac{1}{\rho(E, N)} \tag{5.11}$$

The Gibbs distribution function $\rho(E, N)$ is

$$\rho(E, N) = \frac{\exp[(\mu N - E_{nN})/kT]}{Z_\mu} \tag{5.12}$$

where Z_μ is the grand canonical partition function. Equations (5.10), (5.11) and (5.12) can be rearranged as

$$S = k\ \ln\Big[\exp\Big(\frac{E_{nN} - \mu N}{kT}\Big)\ Z_\mu\Big] = \frac{E_{nN}}{T} - \frac{\mu N}{T} + k\ \ln(Z_\mu)$$

Thus,

$$E_{nN} - ST - \mu\ N = -kT\ \ln(Z_\mu) \qquad \text{or} \qquad \Omega = -kT\ \ln(Z_\mu)$$

where $\Omega = E_{nN} - ST - \mu N = F - \mu N$ is known as the 'thermodynamic potential' or often called the 'grand potential'. Here, the mean energy is the internal energy $U = E_{nN}$ and the Helmholtz free energy $F = E_{nN} - ST$. We can now calculate various thermodynamic quantities in a grand canonical ensemble.

(i) Pressure P of the system is

$$P = -\frac{\partial\Omega}{\partial V} = kT\ \frac{\partial}{\partial V}(\ln Z_\mu)$$

(ii) Entropy S of the system is

$$S = -\frac{\partial \Omega}{\partial T} = k\ \frac{\partial}{\partial T}(T\ \ln Z_\mu) = k\ \ln Z_\mu + kT\ \frac{\partial}{\partial T}(\ln Z_\mu)$$

(iii) Average number of particles N is

$$N = -\frac{\partial \Omega}{\partial \mu} = kT\ \frac{\partial}{\partial \mu}(\ln Z_\mu)$$

(iv) Helmholtz free energy F of the system is

$$F = \Omega + \mu N = -kT\ \ln(Z_\mu) + \mu N$$

(v) Internal energy U of the system is

$$U = F + ST = \mu N + kT^2\ \frac{\partial}{\partial T}(\ln Z_\mu)$$

(vi) The specific heat at constant volume is

$$c_V = \frac{\partial U}{\partial T} = 2kT\ \frac{\partial}{\partial T}(\ln Z_\mu) + kT^2\ \frac{\partial^2}{\partial T^2}(\ln Z_\mu)$$

4. Classical system in a grand canonical ensemble

Consider a open system comprising N identical particles, each of mass m, enclosed in a volume V at temperature T. The total energy E of the system is

$$E_N(q,p) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(q) \tag{5.13}$$

where p_i's are the momentum coordinates of the particles and $U(q)$ the potential energy of the system. The dimensionless partition function of the system in the grand canonical ensemble is (equation 5.13)

$$Z_\mu = \sum_N \frac{1}{N!h^{3N}} \Big\{ \exp\Big(\frac{\mu N}{kT}\Big) \int \exp\Big[-\frac{E_N(q,p)}{kT} \Big]\ \mathrm{d}q\ \mathrm{d}p \Big\} \tag{5.14}$$

Using equation (5.13) in (5.14), we get

$$Z_\mu = \sum_N \Big\{ \frac{1}{N!h^{3N}}\ \ \exp\Big(\frac{\mu N}{kT}\Big) \int \exp\Big(-\sum_{i=1}^{3N} \frac{p_i^2}{2mkT} \Big) \exp\Big(-\frac{U}{kT} \Big)\ \mathrm{d}q\ \mathrm{d}p \Big\}$$

$$= \sum_N \Big\{ \frac{1}{N! h^{3N}} \exp\Big(\frac{\mu N}{kT}\Big)\ I_N \Big[\prod_{i=1}^{3N} \int \exp(-p_i^2/2mkT)\ \mathrm{d}p_i \Big] \Big\} \qquad (5.15)$$

where

$$I_N = \int \exp(-U/kT)\ \mathrm{d}q_1\ \ldots\ \mathrm{d}q_{3N}$$

is the configural integral of the system. We have

$$\int_{-\infty}^{\infty} \exp(-p_i^2/2mkT)\ \mathrm{d}p_i = \sqrt{2\pi mkT}$$

Using the value of this integral in equation (5.15), we have

$$Z_\mu = \sum_N \Big[\frac{1}{N!\ h^{3N}} \exp\Big(\frac{\mu N}{kT}\Big)\ (2\pi mkT)^{3N/2}\ I_N \Big]$$

$$= \sum_N \Big[\frac{I_N}{N!}\ \frac{\exp\Big(\mu N/kT\Big)}{\lambda^{3N}} \Big]$$

where $\lambda = h/\sqrt{2\pi mkT}$ is the thermal wavelength. The thermal wavelength having dimension of length depends on the kinetic temperature of the gas.

4.1 Case of an ideal gas

For an ideal gas, the constituent particles do not interact with one another and thus, the potential energy U of the gas is zero and we have

$$I_N = \int \mathrm{d}q_1\ \ldots\ \mathrm{d}q_{3N} = V^N$$

as the integration over three position coordinates of a particle contributes the volume V of the system. Thus, for an ideal gas, the grand canonical partition function is

$$Z_\mu = \sum_N \Big\{ \frac{1}{N!} \Big[\frac{V\ \exp(\mu/kT)}{\lambda^3} \Big]^N \Big\} = \exp\Big[\frac{V\ \exp(\mu/kT)}{\lambda^3} \Big] \qquad (5.16)$$

where we used the relation

$$\sum_{n=0}^{\infty} \frac{y^n}{n!} = \exp(y)$$

This expression can be used to calculate thermodynamic quantities of an ideal gas in grand canonical ensemble. Using equation (5.16) in (5.12), we have

$$\Omega = -kT \ln(Z_\mu) = -\frac{kTV \exp(\mu/kT)}{\lambda^3}$$

(i) Average number of particles N is

$$N = -\frac{\partial \Omega}{\partial \mu} = \frac{V \exp(\mu/kT)}{\lambda^3} \tag{5.17}$$

(ii) Pressure P of the system is

$$P = -\frac{\partial \Omega}{\partial V} = \frac{kT \exp(\mu/kT)}{\lambda^3} \tag{5.18}$$

(iii) Dividing equation (5.17) by (5.18), we get

$$\frac{N}{P} = \frac{V}{kT} \qquad \text{and thus,} \qquad PV = NkT$$

This is the equation of state.

(iv) Entropy S of the system is

$$S = -\frac{\partial \Omega}{\partial T} = \frac{kV \exp(\mu/kT)}{\lambda^3} \left[\frac{5}{2} - \frac{\mu}{kT}\right]$$

(v) Helmholtz free energy

$$F = \Omega + \mu N = \frac{V \exp(\mu/kT)}{\lambda^3} (\mu - kT)$$

(vi) Internal energy

$$U = F + ST = \frac{3}{2} \frac{VkT \exp(\mu/kT)}{\lambda^3}$$

(vii) Specific heat at constant volume is

$$c_V = \frac{\partial U}{\partial T} = \frac{3}{2} \frac{VkT \exp(\mu/kT)}{\lambda^3} \left[\frac{5}{2} - \frac{\mu}{kT}\right]$$

Exercise 1. Calculate thermodynamic quantities of a system comprising non-interacting, identical, linear harmonic oscillators in grand canonical ensemble.

Solution: Let us consider a system comprising N non-interacting, identical, linear harmonic oscillators, each of mass m, in thermal equilibrium at temperature T in grand canonical ensemble. The oscillators do not interact with one another and they are identical. Let us assume that each

of the oscillators executes small oscillations with the same frequency ω. The situation can be dealt in two ways: (A) Classical treatment and (B) Quantum mechanical treatment.

(A) Classical treatment

Total energy of the system of N oscillators is

$$E(q,p) = \sum_{i=1}^{N} \Big[\frac{p_i^2}{2m} + \frac{1}{2}\, m\omega^2 q_i^2\Big] \tag{5.19}$$

where q_i and p_i are position and momentum coordinates of the i-th oscillator, respectively. The partition function of the system is

$$Z_\mu = \sum_N \Big[\frac{1}{N!h^N}\, \exp\Big(\frac{\mu N}{kT}\Big) \int \exp\Big(-\Big\{\sum_{i=1}^{N}\Big[\frac{p_i^2}{2mkT} + \frac{m\omega^2 q_i^2}{2kT}\Big]\Big)\, \mathrm{d}q\, \mathrm{d}p\Big]$$

$$= \sum_N \Big[\frac{1}{N!\, h^N}\, \exp\Big(\frac{\mu N}{kT}\Big) \prod_{i=1}^{N} \Big\{ \int_{-\infty}^{\infty} \exp(-p_i^2/2mkT)\, \mathrm{d}p_i$$

$$\times \int_{-\infty}^{\infty} \exp(-m\omega^2 q_i^2/2kT)\, \mathrm{d}q_i \Big\}\Big] \tag{5.20}$$

We have

$$\int_{-\infty}^{\infty} \exp(-p_i^2/2mkT)\, \mathrm{d}p_i = \sqrt{2\pi mkT} \tag{5.21}$$

and

$$\int_{-\infty}^{\infty} \exp(-m\omega^2 q_i^2/2kT)\, \mathrm{d}q_i = \sqrt{\frac{2\pi kT}{m\omega^2}} \tag{5.22}$$

Using equations (5.21) and (5.22) in (5.20), we get

$$Z_\mu = \sum_N \Big\{\frac{1}{N!h^N}\, \exp\Big(\frac{\mu N}{kT}\Big)\Big(2\pi mkT\Big)^{N/2}\Big(\frac{2\pi kT}{m\omega^2}\Big)^{N/2}\Big\}$$

$$= \sum_N \frac{1}{N!}\Big[\Big(\frac{2\pi kT}{h\omega}\Big)\, \exp\Big(\frac{\mu}{kT}\Big)\Big]^N = \exp\Big[\Big(\frac{2\pi kT}{h\omega}\Big)\, \exp\Big(\frac{\mu}{kT}\Big)\Big] \tag{5.23}$$

where we used the relation

$$\sum_{n=0}^{\infty} \frac{y^n}{n!} = \exp(y)$$

Using equation (5.23) in (5.12), we have

$$\Omega = -kT \ln\Big(Z_\mu\Big) = -\Big(\frac{2\pi k^2T^2}{h\omega}\Big) \exp\Big(\frac{\mu}{kT}\Big) \tag{5.24}$$

This expression can be used to calculate thermodynamic quantities of an ideal gas in grand canonical ensemble.

(i) Average number of particles N is

$$N = -\frac{\partial\Omega}{\partial\mu} = \Big(\frac{2\pi kT}{h\omega}\Big) \exp\Big(\frac{\mu}{kT}\Big)$$

(ii) Entropy S of the system is

$$S = -\frac{\partial\Omega}{\partial T} = \frac{4\pi k^2T}{h\omega} \exp\Big(\frac{\mu}{kT}\Big)\Big[1 - \frac{\mu}{2kT}\Big]$$

(iii) Helmholtz free energy F of the system is

$$F = \Omega + \mu N = \frac{2\pi kT}{h\omega}(\mu - kT) \exp\Big(\frac{\mu}{kT}\Big)$$

(iv) Internal energy U of the system is

$$U = F + ST = \frac{2\pi k^2T^2}{h\omega} \exp\Big(\frac{\mu}{kT}\Big)$$

(v) Specific heat at constant volume

$$c_V = \frac{\partial U}{\partial T} = \frac{2\pi k^2T^2}{h\omega} \exp\Big(\frac{\mu}{kT}\Big)\Big[2 - \frac{\mu}{kT}\Big]$$

(B) Quantum mechanical treatment

In quantum mechanics, energy of an oscillator is quantized and the energy of the oscillator in state n is

$$E_n = \hbar\omega\Big(n + \frac{1}{2}\Big) \tag{5.25}$$

where n can assume all possible integer values $n = 0, 1, 2, 3, \ldots$ The partition function of an oscillator is

$$Z_1 = \exp\Big[\frac{\mu}{kT}\Big] \sum_{n=0}^{\infty} \exp\Big(-E_n/kT\Big) = \exp\Big[\frac{\mu}{kT}\Big] \sum_{n=0}^{\infty} \exp[-\hbar\omega(n + 1/2)/kT]$$

$$= \exp\Big[\frac{\mu}{kT}\Big]\Big[\exp(-\hbar\omega/2kT) + \exp(-3\hbar\omega/2kT) + \exp(-5\hbar\omega/2kT)$$

$$+\exp(-7\hbar\omega/2kT) + \ldots\Big] = \exp\Big[\frac{\mu}{kT}\Big]\frac{\exp(-\hbar\omega/2kT)}{1-\exp(-\hbar\omega/kT)}$$

Thus, the partition function of N particles is

$$Z_N = Z_1^N = \exp\Big[\frac{N\mu}{kT}\Big]\Big[\frac{\exp(-\hbar\omega/2kT)}{1-\exp(-\hbar\omega/kT)}\Big]^N$$

As the number of particles is allowed to change in the grand canonical ensemble, the partition function of the system is

$$Z_\mu = \sum_N Z_N = \sum_N \Big\{\exp\Big(\frac{\mu N}{kT}\Big)\Big[\frac{\exp(-\hbar\omega/2kT)}{1-\exp(-\hbar\omega/kT)}\Big]^N\Big\}$$

$$= \sum_N \Big[\frac{\exp\{(2\mu-\hbar\omega)/2kT\}}{1-\exp(-\hbar\omega/kT)}\Big]^N = \Big[1-\frac{\exp\{(2\mu-\hbar\omega)/2kT\}}{1-\exp(-\hbar\omega/kT)}\Big]^{-1} \quad (5.26)$$

where we used the relation

$$\sum_{i=0}^{\infty} x^i = (1-x)^{-1}$$

Using equation (5.26) in (5.24), we have

$$\Omega = -kT\,\ln\Big(Z_\mu\Big) = -kT\,\ln\Big[1-\frac{\exp\{(2\mu-\hbar\omega)/2kT\}}{1-\exp(-\hbar\omega/kT)}\Big]^{-1}$$

$$= kT\,\ln\Big[1-\frac{\exp\{(2\mu-\hbar\omega)/2kT\}}{1-\exp(-\hbar\omega/kT)}\Big]$$

$$= -kT\sum_{i=1}^{\infty}\frac{1}{i}\Big[\frac{\exp\{(2\mu-\hbar\omega)/2kT\}}{1-\exp(-\hbar\omega/kT)}\Big]^i \quad (5.27)$$

where we used the relation

$$\ln(1-x) = -\sum_{i=1}^{\infty}\frac{x^i}{i}$$

Equation (5.27) can be used to calculate thermodynamic quantities of an ideal gas in grand canonical ensemble.

(i) Average number of particles N is

$$N = -\frac{\partial\Omega}{\partial\mu} = \sum_{i=1}^{\infty}\Big[\frac{\exp\{(2\mu-\hbar\omega)/2kT\}}{1-\exp(-\hbar\omega/kT)}\Big]^i$$

(ii) Entropy S of the system is

$$S = -\frac{\partial \Omega}{\partial T} = \sum_{i=1}^{\infty} \Big\{ \Big[\frac{\exp\{(2\mu - \hbar\omega)/2kT\}}{1 - \exp(-\hbar\omega/kT)} \Big]^i$$

$$\times \Big[\frac{(\hbar\omega - 2\mu + 2kT/i) + (\hbar\omega + 2\mu - 2kT/i)\exp(-\hbar\omega/kT)}{2T\{1 - \exp(-\hbar\omega/kT)\}} \Big] \Big\}$$

(iii) Helmholtz free energy F of the system is

$$F = \Omega + \mu N$$

$$= -kT \sum_{i=1}^{\infty} \frac{1}{i} \Big[\frac{\exp\{(2\mu - \hbar\omega)/2kT\}}{1 - \exp(-\hbar\omega/kT)} \Big]^i + \mu \sum_{i=1}^{\infty} \Big[\frac{\exp\{(2\mu - \hbar\omega)/2kT\}}{1 - \exp(-\hbar\omega/kT)} \Big]^i$$

$$= \sum_{i=1}^{\infty} \Big\{ \Big[\mu - \frac{kT}{i} \Big] \Big[\frac{\exp\{(2\mu - \hbar\omega)/2kT\}}{1 - \exp(-\hbar\omega/kT)} \Big]^i \Big\}$$

(iv) Internal energy U of the system is

$$U = F + ST = \frac{\hbar\omega}{2} \sum_{i=1}^{\infty} \Big[\frac{\exp\{(2\mu - \hbar\omega)/2kT\}}{1 - \exp(-\hbar\omega/kT)} \Big]^i$$

(v) The specific heat at constant volume is

$$c_V = \frac{\hbar\omega}{2} \sum_{i=1}^{\infty} i \Big[\frac{\exp\{(2\mu - \hbar\omega)/2kT\}}{1 - \exp(-\hbar\omega/kT)} \Big]^i \Big[\frac{\hbar\omega - 2\mu}{2kT^2} - \frac{\hbar\omega/kT^2}{\exp(\hbar\omega/kT) - 1} \Big]$$

5. Density and energy fluctuations in a grand canonical ensemble

We know that for a system in a grand canonical ensemble, the energy and the number of constituent particles do not have constant values, but vary. However, the thermodynamic quantities of the system could be obtained by using the mean values of the energy and the number of particles. Such calculations of thermodynamic properties were based on the assumption that the fluctuations of the energy and the number of particles were negligible. As volume in the grand canonical ensemble is constant, fluctuations in the number of particles are directly related to the fluctuations in the density $\rho(= N/V)$.

(i) In the grand canonical ensemble, the mean number of constituent particles is

$$\langle N\rangle = \frac{\sum_N \sum_n N\, \exp[(\mu N - E_{nN})/kT]}{\sum_N \sum_n \exp[(\mu N - E_{nN})/kT]} \tag{5.28}$$

Differentiating equation (5.28) with respect to μ and keeping E_{nN}, N and T constant, we get[2]

$$\Big(\frac{\partial\langle N\rangle}{\partial\mu}\Big)_T = \frac{1}{kT}\Big[\frac{\sum_N \sum_n N^2\, \exp[(\mu N - E_{nN})/kT]}{\sum_N \sum_n \exp[(\mu N - E_{nN})/kT]}$$

$$-\Big\{\frac{\sum_N \sum_n N\, \exp[(\mu N - E_{nN})/kT]}{\sum_N \sum_n \exp[(\mu N - E_{nN})/kT]}\Big\}^2\Big]$$

$$= \frac{1}{kT}[\langle N^2\rangle - \langle N\rangle^2] = \frac{1}{kT}\langle(\Delta N)^2\rangle$$

where ΔN is the fluctuation in the number of particles in the system. Thus,

$$\langle(\Delta N)^2\rangle = kT\Big(\frac{\partial\langle N\rangle}{\partial\mu}\Big)_T$$

(ii) Fluctuation in the energy of the system in grand canonical ensemble can be estimated in the following manner. The the mean energy of constituent particles is

$$U \equiv \langle E\rangle = \frac{\sum_N \sum_n E_{nN}\, \exp[\beta(\mu N - E_{nN})]}{\sum_N \sum_n \exp[\beta(\mu N - E_{nN})]} \tag{5.29}$$

where for convenience we have taken $\beta = 1/kT$. Differentiating equation (5.29) with respect to β and keeping E_{nN}, N and μ constant, we get

$$\frac{\partial U}{\partial\beta} = \frac{\sum_N \sum_n E_{nN}(\mu N - E_{nN})\, \exp[\beta(\mu N - E_{nN})]}{\sum_N \sum_n \exp[\beta(\mu N - E_{nN})]}$$

$$-\frac{\sum_N \sum_n E_{nN}\, \exp[\beta(\mu N - E_{nN})] \sum_N \sum_n (\mu N - E_{nN})\, \exp[\beta(\mu N - E_{nN})]}{\{\sum_N \sum_n \exp[\beta(\mu N - E_{nN})]\}^2}$$

$$= \frac{\sum_N \sum_n \mu N E_{nN}\, \exp[\beta(\mu N - E_{nN})]}{\sum_N \sum_n \exp[\beta(\mu N - E_{nN})]}$$

[2]Differentiation of $f = u/v$ is

$$f' = \frac{vu' - uv'}{v^2} = \frac{u'}{v} - \frac{u}{v}\frac{v'}{v}$$

$$-\frac{\sum_N \sum_n E_{nN}^2 \exp[\beta(\mu N - E_{nN})]}{\sum_N \sum_n \exp[\beta(\mu N - E_{nN})]}$$

$$-\frac{\sum_N \sum_n E_{nN} \exp[\beta(\mu N - E_{nN})] \sum_N \sum_n \mu N \exp[\beta(\mu N - E_{nN})]}{\{\sum_N \sum_n \exp[\beta(\mu N - E_{nN})]\}^2}$$

$$+\frac{\sum_N \sum_n E_{nN} \exp[\beta(\mu N - E_{nN})] \sum_N \sum_n E_{nN} \exp[\beta(\mu N - E_{nN})]}{\{\sum_N \sum_n \exp[\beta(\mu N - E_{nN})]\}^2}$$

$$= -\frac{\sum_N \sum_n E_{nN}^2 \exp[\beta(\mu N - E_{nN})]}{\sum_N \sum_n \exp[\beta(\mu N - E_{nN})]} + \left\{\frac{\sum_N \sum_n E_{nN} \exp[\beta(\mu N - E_{nN})]}{\sum_N \sum_n \exp[\beta(\mu N - E_{nN})]}\right\}^2$$

$$= -[\langle E^2 \rangle - \langle E \rangle^2] = -\langle (\Delta E)^2 \rangle$$

where ΔE is the fluctuation in the energy of particles in the system. Thus,

$$\langle (\Delta E)^2 \rangle = -\frac{\partial U}{\partial \beta} = kT^2 \frac{\partial U}{\partial T}$$

6. Problems and questions

1. Which of the three physical parameters remain conserved in the system of interest in grand canonical ensemble

   N, V, E, T, μ

   Ans. V, T, μ

2. Derive expressions for thermodynamic quantities for grand canonical ensemble.

3. Discuss about the classical system in the grand canonical ensemble.

4. Calculate thermodynamic quantities of a system comprising non-interacting, identical, linear harmonic oscillators in grand canonical ensemble in classical picture.

5. Calculate thermodynamic quantities of a system comprising non-interacting, identical, linear harmonic oscillators in grand canonical ensemble in quantum mechanical picture.

6. Discuss the density and energy fluctuations in a grand canonical ensemble.

7. Write notes on the following

   (i) Grand canonical ensemble

   (ii) Grand canonical partition function

VI. Three Distributions

When constituent particles of a gas do not interact with one another, it is termed as an ideal gas. Potential energy of the ideal gas is zero, and the total energy is the sum of the kinetic energies of its constituent particles. In true sense, there is no ideal gas, but a gas of weakly interacting particles may be considered as an ideal one. A system of gas may belong to one of the following three categories:

(i) Maxwell-Boltzmann system: In this category, the constituent particles of the gas are distinguishable[1] from one another. This system is also known as the classical system, and there is no restriction on the number of particles which can occupy any energy level.

(ii) Fermi-Dirac system: In this category, the constituent particles of the gas are indistinguishable from one another and the spin quantum number of a particle is a half integer, such as, 1/2, 3/2, 5/2, etc. For example, spin quantum number of each of the electron, positron, proton, neutron and μ-meson is 1/2. These particles are known as the Fermi particles or Fermions. For a constituent particle, when the number of Fermi particles is odd number, the system is said to be Fermi system. For example, the boron atom having 15 Fermi particles (5 electrons + 5 protons + 5 neutrons) is a Fermi particle, but the helium atom having 6 Fermi particles (2 electrons + 2 protons + 2 neutrons) is not a Fermi particle. It is a Bose particle or boson. Total wave function of the system is asymmetric under the exchange of coordinates of any two particles, and the particles obey the Pauli exclusion principle that no two particles can occupy a common quantum level.

[1]When the mean separation between the particles is more than the thermal length, the particles are considered to be distinguishable. On the other side, when the mean separation between the particles is less than the thermal length, the particles are considered to be indistinguishable.

(iii) Bose-Einstein system: In this category, the constituent particles of the gas are also indistinguishable from one another, but the spin quantum number of a particle is an integer, such as 0, 1, 2, etc. For example, spin quantum number of each of the photon and π-meson is 1 and each of the α-particle and deuteron nucleus is zero. These particles are known as the Bose particles or bosons. Even a constituent particle having even number of Fermi particles is a boson. For example, the helium atom having 6 Fermi particles (2 electrons + 2 protons + 2 neutrons) is a boson; hydrogen atom having 2 Fermi particles (1 electron + 1 proton) is a boson. Total wave function of the system is symmetric under the exchange of coordinates of any two particles, and the particles do not obey the Pauli exclusion principle so that any number of particles can occupy a common quantum level.

Fermi-Dirac and Bose-Einstein systems obviously belong to the category of quantum systems. The criterion that the particles in a system are distinguishable or non-distinguishable decides whether the system is to be treated as a classical or quantum mechanical. When the mean distance between the particles is larger than the thermal length, we apply classical distribution, and when the thermal length is smaller than the thermal distance, we apply quantum distribution. Further, in the quantum scenario, spin quantum number of particles is the basis of the two different treatments. In the present chapter, we shall discuss about the laws for these three distributions of systems.

1. Maxwell-Boltzmann distribution

Let us consider an isolated system of N identical, distinguishable and weakly interacting particles contained in a volume V at an equilibrium temperature T with total energy U. Here, we do not account for spin quantum number of the particles. Since the particles are weakly interacting with one another, the potential energy of the system is zero and its total energy is the sum of the kinetic energies of the particles. Example of such system is an ideal mono-atomic gas enclosed in a container. Mean separation between the particles is larger than the thermal length and therefore they are distinguishable and any number of particles can occupy any energy level in the system.

Suppose there are l states with energies, E_1, E_2, $\ldots E_l$, in which the particles are distributed.[2] If the number of particles in these states are

[2]Though in the classical mechanics treatment, the variation of energy is contin-

n_1, n_2, $\ldots n_l$, respectively, we have

$$n_1 + n_2 + \ldots + n_l = N \qquad \text{or} \qquad \sum_{i=1}^{l} n_i = N \tag{6.1}$$

and

$$n_1E_1 + n_2E_2 + \ldots + n_lE_l = U \qquad \text{or} \qquad \sum_{i=1}^{l} n_iE_i = U \tag{6.2}$$

The total energy U and the total number of particles N of the system remain conserved. Further, the energies of the levels E_i's remain unchanged. Thus, differentiation of equations (6.1) and (6.2) gives

$$\sum_{i=1}^{l} \mathrm{d}n_i = \mathrm{d}N = 0 \qquad \text{and} \qquad \sum_{i=1}^{l} E_i \ \mathrm{d}n_i = \mathrm{d}U = 0 \tag{6.3}$$

The particles in the system can be distributed among the energy states in a number of ways, keeping in view that there is no restriction to the number of particles to occupy any energy state and there is equal probability for a particle to occupy any of the energy states. The set of the numbers n_1, n_2, $\ldots n_l$ is one of the probable ways of distribution of particles among the states. It shows that in the equilibrium situation, distribution of particles has maximum probability of occurrence. Let us first count the total number W of independent ways to distribute particles among the states corresponding to the set of the numbers n_1, n_2, $\ldots n_l$, and then find the set of the numbers for which W is maximum.

For the first state with energy E_1, let us find out the number of ways in which n_1 particles are chosen from the N distinguishable particles. The number of ways of choosing the first particle, out of N particles is N. After choosing the first particle, we are left with $(N-1)$ particles. The number of ways of choosing the second particle is $(N-1)$. Then we are left with $(N-2)$ particles. The number of ways of choosing the third, fourth, ..., n_1-th particles are $(N-2)$, $(N-3)$, ..., $(N-n_1+1)$. Thus, the number of ways of selecting n_1 particles out of N particles is

$$= N(N-1)N-2)(N-3) \ \ldots \ (N-n_1+1)$$

$$= \frac{N(N-1)N-2)(N-3) \ \ldots \ (N-n_1+1)(N-n_1)!}{(N-n_1)!} = \frac{N!}{(N-n_1)!}$$

uous, we can still assume various energy levels. The energies of the levels may be varying continuously.

This number includes the $n_1!$ arrangements of n_1 particles among themselves. Any sequence of the particles in the state gives the same distribution of n_1 particles. Thus, the number of independent ways of selecting n_1 particles for the first energy state with energy E_1 is

$$W_1 = \frac{N!}{n_1!(N-n_1)!}$$

After selecting n_1 particles for the first energy state, we are left with $(N-n_1)$ particles. In the similar manner as discussed for the first state, the number of independent ways of selecting n_2 particles out of $(N-n_1)$ particles for the second energy state with energy E_2 is

$$W_2 = \frac{(N-n_1)!}{n_2!(N-n_1-n_2)!}$$

Similarly, the number of independent ways of selecting n_3, n_4, ..., n_l particles for the third, fourth, ..., l-th states are, respectively,

$$W_3 = \frac{(N-n_1-n_2)!}{n_3!(N-n_1-n_2-n_3)!}$$

$$W_4 = \frac{(N-n_1-n_2-n_3)!}{n_4!(N-n_1-n_2-n_3-n_4)!}$$

$$\ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots$$

$$\ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots$$

$$W_l = \frac{(N-n_1-n_2\ldots-n_{l-1})!}{n_l!(N-n_1-n_2\ldots-n_l)!}$$

For these numbers W_1, W_2, W_3, ..., W_l, the total number W of distinct ways of obtaining the distribution of the n_1, n_2, $\ldots n_l$ particles among the states with energies, E_1, E_2, $\ldots E_l$, respectively, is the product of them

$$W = W_1 W_2 W_3 \ \ldots \ W_l$$

$$= \frac{N!}{n_1!(N-n_1)!}\frac{(N-n_1)!}{n_2!(N-n_1-n_2)!}\frac{(N-n_1-n_2)!}{n_3!\ (N-n_1-n_2-n_3)!} \ \cdots$$

$$\frac{(N-n_1-n_2\ldots-n_{l-1})!}{n_l!(N-n_1-n_2\ldots-n_l)!} = \frac{N!}{n_1!n_2!\ldots n_l!}$$

Here, we have used the fact that $(N - n_1 - n_2 \ldots - n_l)$ is zero. So far, we have assumed that the energy states are non-degenerate. Suppose, g_1, g_2, …, g_l are degeneracies of the states with energies E_1, E_2, … E_l, respectively. Then, for example, for the i-th energy state with energy E_i containing n_i particles there are g_i levels, and each of the n_i particles can be in any of the g_i levels without any preference. Since we cannot distinguish between these g_i levels, there are g_i choices for each of the n_i particles to occupy these g_i levels. Thus, there are $g_i \,.\, g_i \ldots \{n_i\text{times}\} (= g_i^{n_i})$ ways of arranging n_i particles among the g_i levels. Hence, the states with degeneracies g_1, g_2, …, g_l and n_1, n_2, … n_l particles, respectively, have $g_1^{n_1}$, $g_2^{n_2}$, …, $g_l^{n_l}$ ways of arranging the particles. After accounting for the degeneracies of the states, the total number of arrangements of the particles in the given distribution is

$$W = \frac{N!}{n_1! n_2! \ldots n_l!}\, g_1^{n_1} g_2^{n_2} \ldots g_l^{n_l} = N! \prod_{i=1}^{l} \Big[\frac{g_i^{n_i}}{n_i!}\Big] \tag{6.4}$$

The most probable distribution of N particles among l energy states is that for which the W is the maximum. For mathematical convenience, we take logarithm of W and consider the maximum of $\ln W$. In equation (6.4), n's are the only variables. Thus, we have

$$\mathrm{d} \ln W = 0$$

$$\frac{\partial}{\partial n_1}(\ln W)\, \mathrm{d}n_1 + \frac{\partial}{\partial n_2}(\ln W)\, \mathrm{d}n_2 + \ldots + \frac{\partial}{\partial n_l}(\ln W)\, \mathrm{d}n_l = 0$$

$$\sum_{i=1}^{l} \frac{\partial}{\partial n_i}(\ln W)\, \mathrm{d}n_i = 0$$

This equation along with the equations (6.3) can be written as

$$\sum_{i=1}^{l} \Big[\frac{\partial}{\partial n_i}(\ln W) - \alpha - \beta E_i\Big] \mathrm{d}n_i = 0 \tag{6.5}$$

where α and β are constants of the system. Equation (6.5) must be true for the individual increments $\mathrm{d}n_i$. Hence, for each level, term in the bracket of equation (6.5) must be zero.

$$\frac{\partial}{\partial n_i}(\ln W) - \alpha - \beta E_i = 0 \tag{6.6}$$

Taking logarithm of equation (6.4), we have

$$\ln W = \ln N! + \ln\Big(\prod_{i=1}^{l}\Big[\frac{g_i^{n_i}}{n_i!}\Big]\Big) = \ln N! + \sum_{i=1}^{l}(n_i \ln g_i - \ln n_i!)$$

Using Stirling formula, we have

$$\ln W = N \ln N - N + \sum_{i=1}^{l}(n_i \ln g_i - n_i \ln n_i + n_i) \tag{6.7}$$

Differentiating equation (6.7) with respect to n_i, we get

$$\frac{\partial}{\partial n_i}(\ln W) = \ln g_i - \ln n_i = -\ln\Big(\frac{n_i}{g_i}\Big) \tag{6.8}$$

Using equation (6.8) in (6.6), we have

$$\ln\Big(\frac{n_i}{g_i}\Big) = -\alpha - \beta E_i \qquad \text{or} \qquad n_i = g_i\, \mathrm{e}^{-\alpha}\, \mathrm{e}^{-\beta E_i} \tag{6.9}$$

This is the Maxwell-Boltzmann distribution of the particles among various states.

Exercise 1. A Maxwell-Boltzmann gas has two particles in the i-th state whose degeneracy is three. Find out the number of independent ways of selecting the particles in the state.

Solution: Here, we have $n_i = 2$, $N = 2$ and $g_i = 3$. The number of independent ways W_i of selecting the particles in the i-th state is

$$W_i = N!\,\frac{g_i^{n_i}}{n_i!} = 2!\,\frac{3^2}{2!} = 9$$

Denoting the two distinguishable particles by the alphabets A and B, 9 independent ways of arranging the particles in 3 levels of the state are given in the table below:

	Levels		
Ways	1	2	3
1	A B	-	-
2	-	A B	-
3	-	-	A B
4	A	B	-
5	B	A	-
6	A	-	B
7	B	-	A
8	-	A	B
9	-	B	A

2. Fermi-Dirac distribution

Let us consider an isolated system of N identical, indistinguishable and weakly interacting particles contained in a volume V at an equilibrium temperature T with total energy U. Here, we account for the particles whose spin quantum number is a half integer. These particles are known as the Fermi-particles or fermions. Examples of the fermions are electron, positron, proton, neutron, μ-meson, each of them with the spin quantum number 1/2. Other example can be at atom having odd number of fermions. For example, a boron atom having 15 fermions (5 electrons, 5 protons, 5 protons) is a Fermi-particle. Since the particles are weakly interacting, the potential energy of the system is zero, and its total energy is the sum of the kinetic energies of the particles. Mean separation between the particles is smaller than the thermal length and therefore they are indistinguishable. Further, these particles with a half-integer spin follow the Pauli exclusion principle, which states that two or more particles can never be in a common quantum level. Hence, in any one level we can have only one particle or no particles.

Suppose there are l states with energies, E_1, E_2, $\ldots E_l$, and degeneracies g_1, g_2, …, g_l, respectively, in which the particles are distributed. If the number of particles in these states are, respectively, n_1, n_2, …, n_l, we have

$$n_1 + n_2 + \ldots + n_l = N \qquad \text{or} \qquad \sum_{i=1}^{l} n_i = N \tag{6.10}$$

and

$$n_1E_1 + n_2E_2 + \ldots + n_lE_l = U \qquad \text{or} \qquad \sum_{i=1}^{l} n_iE_i = U \tag{6.11}$$

Total energy U and total number of particles N of the system remain conserved. Further, the energies of the levels E_i's remain unchanged. Thus, differentiation of equations (6.10) and (6.11) gives

$$\sum_{i=1}^{l} \mathrm{d}n_i = \mathrm{d}N = 0 \qquad \text{and} \qquad \sum_{i=1}^{l} E_i \, \mathrm{d}n_i = \mathrm{d}U = 0 \tag{6.12}$$

Following Pauli's exclusion principle, for the i-th state, the number n_i of particles should not be larger than the degeneracy g_i of the state. Figure 1 shows g_i levels of the i-th state in which we want to accommodate n_i

particles.

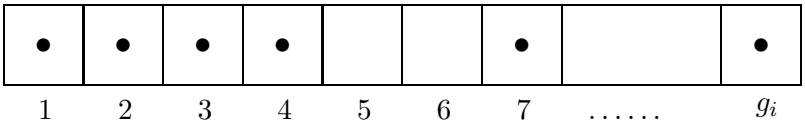

Figure 1: A possible distribution of n_i particles among the levels in the i-th state with degeneracy g_i.

Now, we want to have possible permutations of n_i indistinguishable particles to place in g_i levels with the condition that only one particle or no particle can be placed in each level. The number of ways in which the first of the n_i particles can be placed in one of the g_i levels is g_i. After placing the first particle in one of the g_i levels, the remaining number of levels is $(g_i - 1)$. Thus, the number of ways in which the second particle can be placed in one of the $(g_i - 1)$ levels is $(g_i - 1)$. Similarly, the number of ways in which the third, fourth, ..., n_i-th particles can be placed in one of the remaining levels are $(g_i - 2)$, $(g_i - 3)$, ..., $(g_i - n_i + 1)$.

Thus, the total number of ways of putting n_i particles in g_i levels in the i-th state is

$$= g_i(g_i - 1)(g_i - 2)(g_i - 3)\dots(g_i - n_i + 1)$$

$$= \frac{g_i(g_i - 1)(g_i - 2)(g_i - 3)\dots(g_i - n_i + 1)(g_i - n_i)!}{(g_i - n_i)!} = \frac{g_i!}{(g_i - n_i)!}$$

The number of permutations of n_i particles among themselves is $n_i!$. Because of indistinguishable nature of the particles, these permutations do not give independent arrangements. Thus, the actual number of ways of putting n_i particles in g_i levels in the i-th state is

$$W_i = \frac{g_i!}{n_i!(g_i - n_i)!}$$

For these numbers W_1, W_2, W_3, ..., W_l, for l states, total number W of distinct ways of obtaining the distribution of the particles among the states is the product of them

$$W = W_1 W_2 W_3 \dots W_l$$

$$= \frac{g_1!}{n_1!(g_1 - n_1)!}\frac{g_2!}{n_2!(g_2 - n_2)!}\frac{g_3!}{n_3!(g_3 - n_3)!}\cdots\frac{g_l!}{n_l!(g_l - n_l)!}$$

$$= \prod_{i=1}^{l} \frac{g_i!}{n_i!(g_i - n_i)!} \tag{6.13}$$

The most probable distribution of N particles among l energy states is that for which the W is the maximum. For mathematical convenience, we take logarithm of W and consider the maximum of $\ln W$. In equation (6.13), n's are the only variables. Thus, we have

$$\mathrm{d} \ln W = 0$$

$$\frac{\partial}{\partial n_1}(\ln W)\, \mathrm{d}n_1 + \frac{\partial}{\partial n_2}(\ln W)\, \mathrm{d}n_2 + \ldots + \frac{\partial}{\partial n_l}(\ln W)\, \mathrm{d}n_l = 0$$

$$\sum_{i=1}^{l} \frac{\partial}{\partial n_i}(\ln W)\, \mathrm{d}n_i = 0$$

This equation along with the equations (6.12) can be written as

$$\sum_{i=1}^{l} \Big[\frac{\partial}{\partial n_i}(\ln W) - \alpha - \beta E_i\Big]\mathrm{d}n_i = 0 \tag{6.14}$$

where α and β are constants of the system. Equation (6.14) must be true for the individual increments $\mathrm{d}n_i$. Hence, for each level, term in the bracket of equation (6.14) must be zero.

$$\frac{\partial}{\partial n_i}(\ln W) - \alpha - \beta E_i = 0 \tag{6.15}$$

Taking logarithm of equation (6.13), we have

$$\ln W = \ln\Big[\prod_{i=1}^{l} \frac{g_i!}{n_i!(g_i - n_i)!}\Big] = \sum_{i=1}^{l} \ln\Big[\frac{g_i!}{n_i!(g_i - n_i)!}\Big]$$

$$= \sum_{i=1}^{l} \Big[\ln\, g_i! - \ln\, n_i! - \ln\, (g_i - n_i)!\Big]$$

Using Stirling formula, we have

$$\ln W = \sum_{i=1}^{l} \Big[g_i \ln\, g_i - g_i - n_i \ln\, n_i + n_i - (g_i - n_i)\ln\, (g_i - n_i) + (g_i - n_i)\Big]$$

$$= \sum_{i=1}^{l} \Big[g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i) \Big] \tag{6.16}$$

Differentiating equation (6.16) with respect to n_i, we get

$$\frac{\partial}{\partial n_i}(\ln W) = -\ln n_i + \ln (g_i - n_i) = \ln\Big[\frac{g_i - n_i}{n_i}\Big] \tag{6.17}$$

Using equation (6.17) in (6.15), we have

$$\ln\Big[\frac{g_i - n_i}{n_i}\Big] - \alpha - \beta E_i = 0 \qquad \text{or} \qquad n_i = \frac{g_i}{\mathrm{e}^{(\alpha+\beta E_i)} + 1} \tag{6.18}$$

This is the Fermi-Dirac distribution of the particles among various states.

Exercise 2. A Fermi-Dirac gas has two particles in the i-th state whose degeneracy is three. Find out the number of independent ways of selecting the particles in the state.

Solution: Here, we have $n_i = 2$ and $g_i = 3$. The number of independent ways W_i of selecting the particles in the level is

$$W_i = \frac{g_i!}{n_i!(g_i - n_i)!} = \frac{3!}{2!(3-2)!} = \frac{3!}{2!1!} = 3$$

Denoting the two indistinguishable particles by the alphabets A and A, 3 independent ways of arranging the particles, obeying Pauli's exclusion principle, in 3 levels of the state are given in the table below:

	Levels		
Ways	1	2	3
1	A	A	-
2	A	-	A
3	-	A	A

3. Bose-Einstein distribution

Let us consider an isolated system of N identical, indistinguishable and weakly interacting particles contained in a volume V at an equilibrium temperature T with total energy U. Here, we account for the particles whose spin quantum number is an integer. These particles are known as Bose-particles or bosons. Examples of bosons are photon, π-meson, each of them with the spin quantum number 1; α-particle, deuteron nucleus, each of them with the spin quantum number 0. Other example can be at atom having even number of fermions. For example, a carbon atom

having 18 fermions (6 electrons, 6 protons, 6 protons) is a Bose-particle. Since the particles are weakly interacting, the potential energy of the system is zero, and its total energy is the sum of the kinetic energies of the particles. Mean separation between the particles is smaller than the thermal length and therefore they are indistinguishable. Further, these particles with an integer spin do not follow the Pauli's exclusion principle and any number of particles can be in a common level.

Suppose there are l states with energies, E_1, E_2, $\ldots E_l$, and degeneracies g_1, g_2, ..., g_l, respectively, in which the particles are distributed. If the number of particles in these levels are, respectively, n_1, n_2, $\ldots n_l$, we have

$$n_1 + n_2 + \ldots + n_l = N \qquad \text{or} \qquad \sum_{i=1}^{l} n_i = N \tag{6.19}$$

and

$$n_1 E_1 + n_2 E_2 + \ldots + n_l E_l = U \qquad \text{or} \qquad \sum_{i=1}^{l} n_i E_i = U \tag{6.20}$$

Total energy U and total number of particles N of the system remain conserved. Further, the energies of the levels E_i's remain unchanged. Thus, differentiation of equations (6.19) and (6.20) gives

$$\sum_{i=1}^{l} \mathrm{d}n_i = \mathrm{d}N = 0 \qquad \text{and} \qquad \sum_{i=1}^{l} E_i \; \mathrm{d}n_i = \mathrm{d}U = 0 \tag{6.21}$$

Figure 2 shows g_i quantum levels of the i-th state in which we want to accommodate n_i particles.

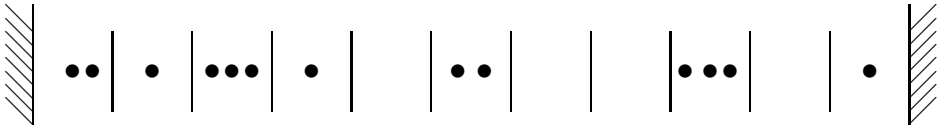

Figure 2: One of the possible distributions of 13 particles among 11 levels with 10 partitions.

Now, we want to have possible permutations of n_i indistinguishable particles to place in g_i levels with the freedom that any number of particles can be placed in any level. For arranging n_i particles in g_i levels, we require $(g_i - 1)$ partitions as shown in Figure 2. The number of permutations of n_i particles among g_i levels is equal to the number of permutations of n_i particles and $(g_i - 1)$ partitions. Obviously, we shall

obtain all possible permutations of the particles plus the partitions, *i.e.*, of $n_i + (g_i - 1)$ objects.

The number of ways of arranging $(n_i + g_i - 1)$ objects is $(n_i + g_i - 1)!$. Here, the number of permutations of n_i particles among themselves is $n_i!$, and that of $(g_i - 1)$ partitions among themselves is $(g_i - 1)!$. Since the particles among themselves and the partitions among themselves are indistinguishable, the number of independent permutations of n_i particles in g_i levels is

$$W_i = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

For these numbers W_1, W_2, W_3, ..., W_l, for l states, total number W of distinct ways of obtaining the distribution of the particles among the states is the product of them

$$\begin{aligned} W &= W_1 W_2 W_3 \ldots W_l \\ &= \frac{(n_1 + g_1 - 1)!}{n_1!(g_1 - 1)!} \frac{(n_2 + g_2 - 1)!}{n_2!(g_2 - 1)!} \frac{(n_3 + g_3 - 1)!}{n_3!(g_3 - 1)!} \cdots \frac{(n_l + g_l - 1)!}{n_l!(g_l - 1)!} \\ &= \prod_{i=1}^{l} \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \end{aligned}$$

Since n_i and g_i are large numbers, we can omit 1 in comparison to them, and we have

$$W = \prod_{i=1}^{l} \frac{(n_i + g_i)!}{n_i!\ g_i!} \tag{6.22}$$

The most probable distribution of N particles among l states is that for which the W is the maximum. For mathematical convenience, we take logarithm of W and consider the maximum of $\ln W$. In equation (6.22), n's are the only variables. Thus, we have

$$\begin{aligned} &\mathrm{d} \ln W = 0 \\ &\frac{\partial}{\partial n_1}(\ln W)\ \mathrm{d}n_1 + \frac{\partial}{\partial n_2}(\ln W)\ \mathrm{d}n_2 + \ldots + \frac{\partial}{\partial n_l}(\ln W)\ \mathrm{d}n_l = 0 \\ &\sum_{i=1}^{l} \frac{\partial}{\partial n_i}(\ln W)\ \mathrm{d}n_i = 0 \end{aligned}$$

This equation along with equations (6.21) can be written as

$$\sum_{i=1}^{l} \Big[\frac{\partial}{\partial n_i}(\ln W) - \alpha - \beta E_i\Big] \mathrm{d}n_i = 0 \tag{6.23}$$

where α and β are constants of the system. Equation (6.23) must be true for the individual increments $\mathrm{d}n_i$. Hence, for each level, term in the bracket of equation (6.23) must be zero.

$$\frac{\partial}{\partial n_i}(\ln\, W) - \alpha - \beta\; E_i = 0 \tag{6.24}$$

Taking logarithm of equation (6.22), we have

$$\ln\, W = \ln\Big[\prod_{i=1}^{l} \frac{(n_i + g_i)!}{n_i!\; g_i!}\Big] = \sum_{i=1}^{l} \ln\Big[\frac{(n_i + g_i)!}{n_i!\; g_i!}\Big]$$
$$= \sum_{i=1}^{l} \Big[\ln\, (n_i + g_i)! - \ln\, n_i! - \ln\, g_i!\Big]$$

Using Stirling formula, we have

$$\ln\, W = \sum_{i=1}^{l} \Big[(n_i + g_i)\ln\, (n_i + g_i) - (n_i + g_i) - n_i \ln\, n_i + n_i - g_i \ln\, g_i + g_i\Big]$$

$$= \sum_{i=1}^{l} \Big[(n_i + g_i)\, \ln\, (n_i + g_i) - n_i\, \ln\, n_i - g_i\, \ln\, g_i\Big] \tag{6.25}$$

Differentiating equation (6.25) with respect to n_i, we get

$$\frac{\partial}{\partial n_i}(\ln\, W) = \frac{n_i + g_i}{n_i + g_i} + \ln\, (n_i + g_i) - \frac{n_i}{n_i} - \ln\, n_i - 0$$

$$= \ln\, (g_i + n_i) - \ln\, n_i = \ln\Big[\frac{n_i + g_i}{n_i}\Big] \tag{6.26}$$

Using equation (6.26) in (6.24), we have

$$\ln\Big[\frac{n_i + g_i}{n_i}\Big] - \alpha - \beta\; E_i = 0 \qquad \text{or} \qquad n_i = \frac{g_i}{\mathrm{e}^{(\alpha + \beta E_i)} - 1} \tag{6.27}$$

This is the Bose-Einstein distribution of the particles among various states.

Exercise 3. A Bose-Einstein gas has two particles in the i-th state whose degeneracy is three. Find out the number of independent ways of selecting the particles in the state.

Solution: Here, we have $n_i = 2$ and $g_i = 3$. The number of independent ways W_i of selecting the particles in the state is

$$W_i = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} = \frac{(2 + 3 - 1)!}{2!(3 - 1)!} = \frac{4!}{2!\; 2!} = 6$$

Denoting the two indistinguishable particles by the alphabets A and A, 6 independent ways of arranging the particles in 3 levels of the state are given in the table below:

	Levels		
Ways	1	2	3
1	A A	-	-
2	-	A A	-
3	-	-	A A
4	A	A	-
5	A	-	A
6	-	A	A

Exercise 4. The energy ϵ of an oscillator with frequency ν is

$$\epsilon = \Big(n + \frac{1}{2}\Big)h\nu \qquad \text{where} \qquad n = 0, 1, 2, \ldots$$

When a system consisting of N independent oscillators has a total energy

$$E = \frac{1}{2}\ Nh\nu + Mh\nu$$

find out (i) statistical weight W_i, and (ii) relation between the temperature T and energy E of this system.

Solution: (i) When we denote quantum number of the i-th state by n_i, the statement that the total energy of the system is equal to $\frac{1}{2}Nh\nu + Mh\nu$ shows that

$$n_1 + n_2 + \ldots + n_N = M$$

and the number of quantum levels is N. Thus, from section 3 (Bose Einstein Distribution), we have

$$W_i = \frac{(M + N - 1)!}{M!(N - 1)!}$$

(ii) The entropy of the system is

$$S = k\ \ln W_i$$

Substituting W_i and using Sterling formula under the assumption that $N >> 1$ and $M >> 1$, we get

$$S = k\Big[(M + N)\ \ln(M + N) - M\ \ln M - N\ \ln N\Big]$$

The temperature T is the system is

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial M}\,\frac{\partial M}{\partial E} = k\,\ln\Big(\frac{M+N}{M}\Big)\,\frac{\partial M}{\partial E}$$

$$= \frac{k}{h\nu}\,\ln\Big(\frac{M+N/2+N/2}{M+N/2-N/2}\Big) = \frac{k}{h\nu}\,\ln\Big(\frac{E/N+h\nu/2}{E/N-h\nu/2}\Big)$$

or

$$\frac{E+Nh\nu/2}{E-Nh\nu/2} = \exp(h\nu/kT)$$

On solving this for E, one get

$$E = N\,\Big(\frac{1}{2}\,h\nu + \frac{h\nu}{\exp(h\nu/kT)-1}\Big)$$

This is the required relation between the temperature T and energy E of the system.

Exercise 5. Show that the Maxwell-Boltzmann distribution is the limiting case of the Fermi-Dirac and Bose-Einstein distributions, and the Maxwell-Boltzmann distribution is applicable to the rarefied gases.

Solution: The three distributions can be expressed as

$$n_i = \frac{g_i}{\mathrm{e}^{(\alpha+\beta E_i)}+J}$$

where

$$J = \begin{cases} 0 & \text{for Maxwell-Boltzmann distribution} \\ 1 & \text{for Fermi-Dirac distribution} \\ -1 & \text{for Bose-Einstein distribution} \end{cases}$$

Obviously, when

$$\mathrm{e}^{(\alpha+\beta E_i)} >> 1 \tag{6.28}$$

the Fermi-Dirac as well as the Bose-Einstein distributions reduce to the Maxwell-Boltzmann distribution. Hence, the Maxwell-Boltzmann distribution is the limiting case of the Fermi-Dirac and Bose-Einstein distributions. For the Maxwell-Boltzmann distribution we have

$$\frac{n_i}{g_i} = \frac{1}{\mathrm{e}^{(\alpha+\beta E_i)}} \tag{6.29}$$

Equations (6.28) and (6.29) give

$$\frac{n_i}{g_i} << 1$$

It shows that in the Maxwell-Boltzmann gas the number of particles per level are very less. Hence, the Maxwell-Boltzmann distribution is applicable to a rarefied gas.

Exercise 6. For Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein distributions, the total number W of distinct ways of obtaining the distribution of the n_1, n_2, $\ldots n_l$ particles among the states with energies, E_1, E_2, $\ldots E_l$, with degeneracies g_1, g_2, $\ldots$, g_l, respectively, are

$$W = N! \prod_{i=1}^{l} \Big[\frac{g_i^{n_i}}{n_i!}\Big] \qquad W = \prod_{i=1}^{l} \frac{g_i!}{n_i!(g_i - n_i)!} \qquad W = \prod_{i=1}^{l} \frac{(n_i + g_i)!}{n_i! g_i!}$$

Calculate entropy of gas in the three distributions.

Solution: Entropy S of the gas, defined as $S = k\ \ln W$, is obtained as the following. For Maxwell-Boltzmann distribution, we have

$$S = k\ \ln W = k\Big[N\ \ln\ N - N + \sum_{i=1}^{l} (n_i\ \ln\ g_i - n_i\ \ln\ n_i + n_i)\Big]$$

$$= k\ \sum_{i=1}^{l} n_i(\ln\ N + \ln\ g_i - \ln\ n_i) = k \sum_{i=1}^{l} \ln\Big(\frac{N g_i}{n_i}\Big)^{n_i}$$

For Fermi-Dirac distribution, we have

$$S = k\ \ln W = k \sum_{i=1}^{l} [g_i\ \ln\ g_i - n_i\ \ln\ n_i - (g_i - n_i)\ \ln\ (g_i - n_i)]$$

$$= k \sum_{i=1}^{l} \Big[n_i\ \ln\Big(\frac{g_i - n_i}{n_i}\Big) - g_i\ \ln\Big(\frac{g_i - n_i}{g_i}\Big)\Big]$$

$$= k \sum_{i=1}^{l} \Big[n_i\ \ln\Big(\frac{g_i}{n_i} - 1\Big) - g_i\ \ln\Big(1 - \frac{n_i}{g_i}\Big)\Big]$$

For Bose-Einstein distribution, we have

$$S = k\ \ln W = k \sum_{i=1}^{l} \Big[(n_i + g_i)\ \ln\ (n_i + g_i) - n_i\ \ln\ n_i - g_i\ \ln\ g_i\Big]$$

$$= k \sum_{i=1}^{l} \Big[n_i \ln\Big(\frac{g_i + n_i}{n_i}\Big) + g_i \ln\Big(\frac{g_i + n_i}{g_i}\Big)\Big]$$

$$= k \sum_{i=1}^{l} \Big[n_i \ln\Big(\frac{g_i}{n_i} + 1\Big) + g_i \ln\Big(1 + \frac{n_i}{g_i}\Big)\Big]$$

Exercise 7. For Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein distributions, we have

$$\frac{g_i}{n_i} = \mathrm{e}^{(\alpha + \beta E_i)} + J$$

where

$$J = \begin{cases} 0 & \text{for Maxwell-Boltzmann distribution} \\ 1 & \text{for Fermi-Dirac distribution} \\ -1 & \text{for Bose-Einstein distribution} \end{cases}$$

Find out values of the constants α and β.

Solution: Since the values of α and β do not depend on the distribution, we consider the simple case of Maxwell-Boltzmann distribution, so that

$$n_i = g_i \ \mathrm{e}^{-\alpha} \ \mathrm{e}^{-\beta E_i} \tag{6.30}$$

Average energy of particles in an ideal gas is

$$\bar{E} = \frac{E}{N} = \frac{\sum_{i=1}^{l} n_i E_i}{\sum_{i=1}^{l} n_i}$$

Using equation (6.30), we have

$$\bar{E} = \frac{\sum_{i=1}^{l} E_i g_i \ \mathrm{e}^{-\alpha} \ \mathrm{e}^{-\beta E_i}}{\sum_{i=1}^{l} g_i \ \mathrm{e}^{-\alpha} \ \mathrm{e}^{-\beta E_i}} = \frac{\sum_{i=1}^{l} E_i g_i \ \mathrm{e}^{-\beta E_i}}{\sum_{i=1}^{l} g_i \ \mathrm{e}^{-\beta E_i}}$$

When energy levels are closely packed, we can consider it as a continuum. Then, E_i is replaced by E, g_i by $g(E)$, and summation over the energy states by the integration over the energy. Thus, we have

$$\bar{E} = \frac{\int E g(E) \ \mathrm{e}^{-\beta E} \mathrm{d}E}{\int g(E) \ \mathrm{e}^{-\beta E} \mathrm{d}E}$$

For the particles with no spin, we have (see appendix)

$$g(E) \ \mathrm{d}E = 2\pi V \Big(\frac{2\ m}{h^2}\Big)^{3/2} E^{1/2} \ \mathrm{d}E$$

Using this relation, the average energy is

$$\bar{E} = \frac{\int E^{3/2} 2\pi V (2m/h^2)^{3/2}\ \mathrm{e}^{-\beta E}\mathrm{d}E}{\int E^{1/2} 2\pi V (2m/h^2)^{3/2} \mathrm{e}^{-\beta E}\mathrm{d}E} = \frac{\int E^{3/2}\ \mathrm{e}^{-\beta E}\mathrm{d}E}{\int E^{1/2}\ \mathrm{e}^{-\beta E}\mathrm{d}E} \qquad (6.31)$$

We have

$$\int_0^\infty E^{3/2}\mathrm{e}^{-\beta E}\mathrm{d}E = \frac{3\sqrt{\pi}}{4\beta^{5/2}} \qquad \text{and} \qquad \int_0^\infty E^{1/2}\mathrm{e}^{-\beta E}\mathrm{d}E = \frac{\sqrt{\pi}}{2\beta^{3/2}}$$

Using these relations in equation (6.31), we get

$$\bar{E} = \frac{3}{2\beta} \qquad (6.32)$$

We know that average energy of particles at temperature T is $kT/2$ per degree of freedom. Therefore,

$$\bar{E} = \frac{3}{2}\ kT \qquad (6.33)$$

From equations (6.32) and (6.33), we have

$$\frac{3}{2}\ kT = \frac{3}{2\ \beta} \qquad \text{or} \qquad \beta = \frac{1}{kT}$$

Total number of particles in an ideal gas is

$$N = \sum_{i=1}^{l} n_i = \sum_{i=1}^{l} g_i\ \mathrm{e}^{-\alpha}\ \mathrm{e}^{-\beta E_i}$$

When energy levels are closely packed, we can consider it as a continuum. Then, E_i is replaced by E, g_i by $g(E)$, and summation over the energy states by the integration over the energy. Thus, we have

$$N = \mathrm{e}^{-\alpha} \int_0^\infty g(E)\ \mathrm{e}^{-\beta E}\mathrm{d}E$$

Using the expression for $g(E)\ \mathrm{d}E$, we have

$$N = \mathrm{e}^{-\alpha} 2\pi V \Big(\frac{2m}{h^2}\Big)^{3/2} \int_0^\infty E^{1/2}\ \mathrm{e}^{-\beta E}\mathrm{d}E$$

$$= \mathrm{e}^{-\alpha} 2\pi V \Big(\frac{2m}{h^2}\Big)^{3/2} \frac{\sqrt{\pi}}{2\beta^{3/2}} = \mathrm{e}^{-\alpha} V \Big(\frac{2\pi m}{h^2\beta}\Big)^{3/2}$$

Using $\beta = (1/kT)$ here and on rearranging, we get

$$\mathrm{e}^{-\alpha} = \frac{N}{V}\Big(\frac{h^2}{2\pi m k T}\Big)^{3/2}$$

Using the values of β and $e^{-\alpha}$ in equation (6.30), we have

$$n_i = g_i \frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} e^{-E_i/kT}$$

Exercise 8. Classify the following particles according to Fermi-Dirac or Bose-Einstein statistics:

α-particle, ^{3}He, H_2 Molecule, positron, $^6Li^+$ ion and $^7Li^+$ ion

Solution: Proton (P), neutron (N), electron (e^-), positron (e^+) have half spin and therefore follow the Fermi-Dirac statistics. One can easily classify a given particle by calculating how many Fermi particles are in the given particle. When the total number of Fermi particles there is odd, the given particle is known as the Fermi particle and it follows the Fermi-Dirac statistics. On the other side, when the total number of Fermi particles is even, the particle is known as the Bose particle and it follows the Bose-Einstein statistics.

α-particle : 2 P + 2 N : Total No of Fermi particle = 4 : Bose particle

^{3}He : 2 P + 1 N + 2 e^- : Total No of Fermi particle = 5 : Fermi particle

H_2 Molecule : 2 P + 2 e^- : Total No of Fermi particle = 4 : Bose particle

positron : 1 e^+ : Total No of Fermi particle = 1 : Fermi particle

$^6Li^+$ ion : 3 P + 3 N + 2 e^- : Total No of Fermi particle = 8 : Bose particle

$^7Li^+$ ion : 3 P + 4 N + 2 e^- : Total No of Fermi particle = 9 : Fermi particle

4. Condition for applicability of M-B distribution

The Maxwell-Boltzmann distribution is applicable to a gas of non-interacting, identical, neutral particles. Though the particles are assumed not to interact directly, but they do interact during collisions, otherwise thermal equilibrium will not be maintained. Whether the neutral particles in a system interact or not with one another can be decided by calculating their de Broglie wavelength. When the de Broglie wavelength λ of a particle is smaller than the mean distance d between the particles, the particles will not interact. Thus, the condition for application of

Maxwell-Boltzmann distribution is

$$\lambda \langle d \tag{6.34}$$

For the gas having N particles enclosed in a volume V. The volume per particle is V/N. For this volume, length of one side of a cube is $(V/N)^{1/3}$. Hence, the mean distance between the particles is

$$d = \Big(\frac{V}{N}\Big)^{1/3}$$

For non-interacting particles, the mean energy is $3kT/2$. The corresponding moment p of the particle is

$$E = \frac{3}{2}\, kT \qquad \text{or} \qquad \frac{p^2}{2m} = \frac{3}{2}\, kT$$

Thus, $p = \sqrt{3mkT}$. The corresponding de Broglie wavelength is

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{3mkT}}$$

Substituting values of d and λ in equation (6.34), we get

$$\frac{h}{\sqrt{3mkT}} \;\langle\; \Big(\frac{V}{N}\Big)^{1/3} \qquad \text{or} \qquad \Big(\frac{h^2}{3mkT}\Big)^{3/2}\, \frac{N}{V} \;\langle\; 1$$

Multiplying this relation by $(3/2\pi)^{3/2}$, we get

$$\Big(\frac{3}{2\pi}\Big)^{3/2}\Big(\frac{h^2}{3mkT}\Big)^{3/2}\frac{N}{V} \;\langle\; \Big(\frac{3}{2\pi}\Big)^{3/2} \qquad \text{or} \qquad \Big(\frac{h^2}{2\pi mkT}\Big)^{3/2}\frac{N}{V} \;\langle\; 0.33$$

The required condition therefore is $\mathrm{e}^{-\alpha} << 1$. That is

$$\frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} << 1$$

Thus, the Maxwell-Boltzmann distribution is applicable at large temperatures.

5. Problems and questions

1. Discuss the Maxwell-Boltzmann distribution, and obtain the condition for its application. A Maxwell-Boltzmann gas has two particles in the i-th state whose degeneracy is three. Find the number of independent ways of selecting the particles in the state.

2. Discuss the Fermi-Dirac distribution. A Fermi-Dirac gas has two particles in the i-th state whose degeneracy is three. Find the number of independent ways of selecting the particles in the state.

3. Discuss the Bose-Einstein distribution. A Bose-Einstein gas has two particles in the i-th state whose degeneracy is three. Find the number of independent ways of selecting the particles in the state.

4. In a gas of identical, weakly interacting particles, i-th state with degeneracy 4 has 3 particles. Find the number of ways of selecting the particles in the state under (i) Maxwell-Boltzmann distribution, (ii) Fermi-Dirac distribution and (iii) Bose-Einstein distribution.

   (i) 64, (ii) 4, (iii) 20

5. In a gas of identical, weakly interacting particles, i-th state with degeneracy 5 has 3 particles. Find the number of ways of selecting the particles in the state under (i) Maxwell-Boltzmann distribution, (ii) Fermi-Dirac distribution and (iii) Bose-Einstein distribution.

   (i) 125, (ii) 10, (iii) 35

6. Obtain condition for application of Maxwell-Boltzmann distribution. Show that Maxwell-Boltzmann distribution is the limiting case of Fermi-Dirac and Bose-Einstein distributions, and the Maxwell-Boltzmann distribution is applicable to rarefied gases.

7. For the Maxwell-Boltzmann distribution of the particles

$$n_i = g_i \, \mathrm{e}^{(-\alpha - \beta E_i)}$$

   obtain expressions for α and β.

8. Derive a condition for application of the Maxwell-Boltzmann distribution.

9. Derive expressions for entropy in the three distributions.

10. Which of the followings is fermion.

    (i) photon (ii) hydrogen (iii) helium (iv) boron

    Ans. (iv)

11. Write notes on the following

    (i) Maxwell-Boltzmann distribution

(ii) Fermi-Dirac distribution

(iii) Bose-Einstein distribution

(iv) Condition for application of Maxwell-Boltzmann distribution

VII. Maxwell-Boltzmann System

Consider a gas consisting of N identical, distinguishable particles contained in a volume V at an equilibrium temperature T with total energy U. The thermal length $\lambda = h/\sqrt{2\pi mkT}$ of the system is less than the mean distance between them. For such a gas we do not account for spin quantum number of the particles, and the gas is termed as the Maxwell-Boltzmann gas. When we consider that the particles in the gas are not interacting with each other, then the gas is known as an ideal Maxwell-Boltzmann gas. Hence, the potential energy of the gas is zero and its total energy is equal to the sum of the kinetic energies of the constituent particles.

1. Maxwell-Boltzmann distribution

Suppose there are l states with energies, E_1, E_2, ..., E_l and degeneracies, g_1, g_2, ..., g_l, respectively, in which the particles are distributed. If the numbers of particles in these states are, respectively, n_1, n_2, ..., n_l, the Maxwell-Boltzmann distribution law for the particles in the states is

$$n_i = g_i \, \mathrm{e}^{-\alpha} \, \mathrm{e}^{-\beta E_i}$$

After using the values

$$\mathrm{e}^{-\alpha} = \frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} \qquad \text{and} \qquad \beta = \frac{1}{kT}$$

we get

$$n_i = g_i \, \frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} \mathrm{e}^{-E_i/kT}$$

1.1 Energy distribution function

Energy distribution function $f(E_i)$ is the average number of particles per level in the energy states E_i. Therefore

$$f(E_i) = \frac{n_i}{g_i} = \frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} \mathrm{e}^{-E_i/kT}$$

Hence,

$$f(E) = \frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} \mathrm{e}^{-E/kT} \tag{7.1}$$

This is known as the Maxwell-Boltzmann energy distribution function for an ideal gas.

1.2 Energy distribution law

The number of particles $n(E)\ \mathrm{d}E$ having energies in the range from E to $E + \mathrm{d}E$ is

$$n(E)\ \mathrm{d}E = f(E)g(E)\ \mathrm{d}E$$

where $g(E)\ \mathrm{d}E$ is the number of levels in the energy range from E to $E + \mathrm{d}E$. Using the expressions for the Maxwell-Boltzmann energy distribution function $f(E)$ and $g(E)\ \mathrm{d}E$, we have

$$n(E)\ \mathrm{d}E = \frac{2\pi N}{(\pi kT)^{3/2}}\ E^{1/2}\mathrm{e}^{-E/kT}\mathrm{d}E \tag{7.2}$$

This is known as the Maxwell-Boltzmann energy distribution law for an ideal gas.

1.3 Partition function

Total number of particles in a gas are

$$N = \sum_{i=1}^{l} n_i = \sum_{i=1}^{l} g_i\ \mathrm{e}^{-\alpha}\mathrm{e}^{-E_i/kT} = \mathrm{e}^{-\alpha}\sum_{i=1}^{l} g_i\ \mathrm{e}^{-E_i/kT} = \mathrm{e}^{-\alpha}Z$$

where

$$Z = \sum_{i=1}^{l} g_i\ \mathrm{e}^{-E_i/kT}$$

is known as the partition function of the system. Hence, $\alpha = \ln(Z/N)$. Using the value of α, the partition function can also be expressed as

$$Z = \frac{N}{\mathrm{e}^{-\alpha}} = V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2} = \frac{V}{\lambda^3} \tag{7.3}$$

where $\lambda = h/\sqrt{2\pi mkT}$ is defined as the thermal wavelength.

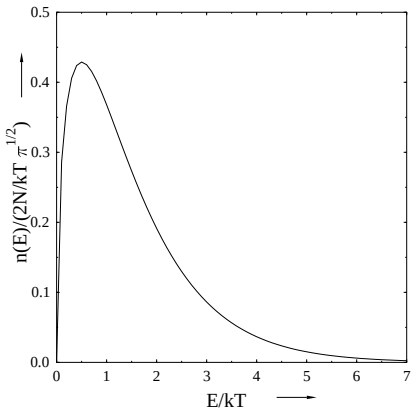

Figure 1: Variation of $n(E)/(2N/kT\pi)$ versus E/kT.

1.4 Most probable energy

For the Maxwell-Boltzmann gas, the number of particles per unit energy range (from equation 7.2) is

$$n(E) = \frac{2\pi N}{(\pi kT)^{3/2}}\ E^{1/2}\ \mathrm{e}^{-E/kT} \tag{7.4}$$

For the given values of N and T, variation of $n(E)/(2N/kT\pi^{1/2})$ as a function of E/kT is shown in Figure 1. The most probable energy is that at which the number of particles per unit energy range is the maximum. For mathematical convenience, let us take logarithm of equation (7.4)

$$\ln\ n(E) = \ln\Big[\frac{2\pi N}{(\pi kT)^{3/2}}\Big] + \frac{1}{2}\ \ln\ E - \frac{E}{kT} \tag{7.5}$$

Differentiating equation (7.5) with respect to E, we get

$$\frac{1}{n(E)}\frac{\mathrm{d}n(E)}{\mathrm{d}E} = \frac{1}{2E} - \frac{1}{kT} \qquad \text{or} \qquad \frac{\mathrm{d}n(E)}{\mathrm{d}E} = n(E)\Big[\frac{1}{2E} - \frac{1}{kT}\Big]$$

At the most probable energy $E = E_p$, $n(E)$ is the maximum, and therefore,

$$\Big[n(E)\Big(\frac{1}{2E} - \frac{1}{kT}\Big)\Big]_{E=E_p} = 0$$

Since $n(E_p) \neq 0$, we have

$$\frac{1}{2E_p} - \frac{1}{kT} = 0 \qquad \text{or} \qquad E_p = \frac{1}{2}\ kT \tag{7.6}$$

The number of particles at E_p are [using equation (7.6) in (7.4)]

$$n(E_p) = \sqrt{\frac{2}{\pi \mathrm{e}}}\ \frac{N}{kT} \tag{7.7}$$

The most probable energy E_p is proportional to the temperature of the gas and is independent of the number of particles in the gas. Hence, with the increase of T, the most probable velocity E_p increases, but the number of particles at E_p decreases. Now, from equations (7.6) and (7.7), we have

$$E_p\ n(E_p) = \frac{N}{\sqrt{2\pi\ \mathrm{e}}}$$

showing that the product of the most probable energy E_p and the number of particles at E_p depend only on the total number N of the particles in the gas. Obviously, with the increase of temperature, the most probable energy E_p increases, but the number of particles at E_p decreases.

1.5 Total number of particles

For the Maxwell-Boltzmann energy distribution law, the total number of particles is

$$\int_0^\infty n(E)\ \mathrm{d}E$$

Using equation (7.4), we have

$$\int_0^\infty n(E)\ \mathrm{d}E = \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^\infty E^{1/2}\ \mathrm{e}^{-E/kT}\ \mathrm{d}E$$

$$= \frac{2\pi N}{(\pi kT)^{3/2}} \frac{\sqrt{\pi}(kT)^{3/2}}{2} = N \tag{7.8}$$

It is the expected value of the number of particles in the gas.

1.6 Average energy

For the Maxwell-Boltzmann energy distribution law, average energy $\overline{E}$ of the particles is

$$\overline{E} = \frac{\int_0^\infty En(E)\ \mathrm{d}E}{\int_0^\infty n(E)\ \mathrm{d}E}$$

Using equations(7.4) and (7.8), we have

$$\overline{E} = \frac{1}{N} \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^\infty E^{3/2} \mathrm{e}^{-E/kT}\ \mathrm{d}E$$

$$= \frac{2\pi}{(\pi kT)^{3/2}} \frac{3\sqrt{\pi}(kT)^{5/2}}{4} = \frac{3}{2}\ kT$$

Hence, the average energy of a particle is $kT/2$ per degree of freedom.

2. Maxwell-Boltzmann velocity distribution law

Maxwell-Boltzmann velocity distribution law can be obtained from the Maxwell-Boltzmann energy distribution law (equation 7.2). For a particle of mass m moving with velocity v, its energy E is

$$E = \frac{1}{2}\, mv^2 \qquad \text{and therefore,} \qquad \mathrm{d}E = mv\ \mathrm{d}v \tag{7.9}$$

Here, we are considering that the interaction between the constituent particles is so weak that the potential energy of the gas is zero. Using equation (7.9) in (7.1), the number of particles having velocity in the range from v to $v + \mathrm{d}v$ is

$$n(v)\ \mathrm{d}v = n(E)\ \mathrm{d}E = 4\pi N\Big(\frac{m}{2\pi kT}\Big)^{3/2} v^2 \mathrm{e}^{-mv^2/2kT}\mathrm{d}v \tag{7.10}$$

This is known as the Maxwell-Boltzmann velocity distribution law.

2.1 Total number of particles

For the Maxwell-Boltzmann velocity distribution law, total number of particles is

$$\int_0^\infty n(v)\ \mathrm{d}v$$

Using equation (7.10), we have

$$\int_0^\infty n(v)\ \mathrm{d}v = 4\pi N\Big(\frac{m}{2\pi kT}\Big)^{3/2} \int_0^\infty v^2 \mathrm{e}^{-mv^2/2kT}\ \mathrm{d}v$$

$$= 4\pi N\Big(\frac{m}{2\pi kT}\Big)^{3/2}\ \frac{2kT}{4m}\sqrt{\frac{2\pi kT}{m}} = N \tag{7.11}$$

It is the expected value for the number of particles in the gas.

2.2 Most probable velocity

The number of particles per unit velocity range (from equation 7.10) is

$$n(v) = 4\pi N\Big(\frac{m}{2\pi kT}\Big)^{3/2} v^2 \mathrm{e}^{-mv^2/2kT} \tag{7.12}$$

Variation of $n(v)/(4N\sqrt{m/2\pi kT})$ as a function of $mv^2/2kT$ is shown in Figure 2. The most probable velocity is that at which the number of

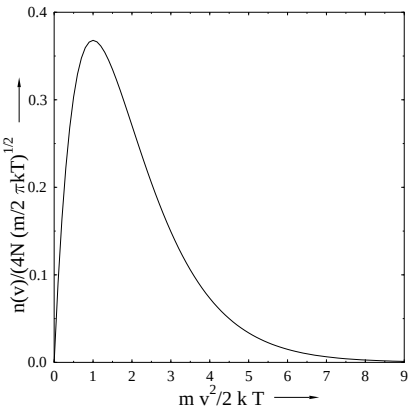

Figure 2: Variation of $n(v)/(4N\sqrt{m/2\pi kT})$ versus $mv^2/2kT$.

particles per unit range is the maximum. For mathematical convenience, let us take logarithm of equation (7.12)

$$\ln\, n(v) = \ln\Big[4\pi N\Big(\frac{m}{2\pi kT}\Big)^{3/2}\Big] + 2\,\ln\, v - \frac{mv^2}{2kT} \tag{7.13}$$

Differentiating equation (7.13) with respect to v, we get

$$\frac{\mathrm{d}n(v)}{\mathrm{d}v} = n(v)\Big[\frac{2}{v} - \frac{mv}{kT}\Big]$$

At the most probable energy $v = v_p$, $n(v)$ is the maximum, and therefore,

$$\Big[\frac{\mathrm{d}n(v)}{\mathrm{d}v}\Big]_{v=v_p} = 0$$

Thus,

$$\Big[n(v)\Big(\frac{2}{v} - \frac{mv}{kT}\Big)\Big]_{v=v_p} = 0$$

Since $n(v_p) \neq 0$, we have

$$\frac{2}{v_p} - \frac{mv_p}{kT} = 0 \qquad \text{or} \qquad v_p = \sqrt{\frac{2kT}{m}} = 1.414\sqrt{\frac{kT}{m}}$$

The number of particles at v_p are [using expression for v_p in equation (7.12)]

$$n(v_p) = \frac{4N}{\mathrm{e}}\sqrt{\frac{m}{2\pi kT}}$$

The most probable velocity v_p is proportional to the square root of temperature of the gas and is independent of the number of particles in

the gas. Hence, with the increase of T, the most probable velocity v_p increases, but the number of particles at v_p decreases. Now, we have

$$v_p \; n(v_p) = \frac{4N}{\mathrm{e}\sqrt{\pi}}$$

showing that the product of the most probable velocity v_p and the number of particles at v_p depend only on the total number N of the particles in the gas. Obviously, with the increase of temperature, the most probable velocity $v_p$increases, but the number of particles at v_p decreases.

2.3 Average velocity

For the Maxwell-Boltzmann velocity distribution law, average velocity of the particles is

$$\overline{v} = \frac{\int_0^\infty v n(v) \; \mathrm{d}v}{\int_0^\infty n(v) \; \mathrm{d}v}$$

Using equations (7.10) and (7.11) here, we have

$$\overline{v} = \frac{1}{N} \; 4\pi N \Big(\frac{m}{2\pi kT}\Big)^{3/2} \int_0^\infty v^3 \mathrm{e}^{-mv^2/2kT} \; \mathrm{d}v$$

$$= 4\pi \Big(\frac{m}{2\pi kT}\Big)^{3/2} \; \frac{1}{2} \Big(\frac{2kT}{m}\Big)^2 = \sqrt{\frac{8kT}{\pi m}} = 1.596 \sqrt{\frac{kT}{m}}$$

2.4 Root mean square velocity

For the Maxwell-Boltzmann velocity distribution law, root mean square velocity v_{rms} of the particles is

$$v_{\mathrm{rms}}^2 = \langle v^2 \rangle = \frac{\int_0^\infty v^2 n(v) \; \mathrm{d}v}{\int_0^\infty n(v) \; \mathrm{d}v}$$

Using equations (7.10) and (7.11) here, we have

$$v_{\mathrm{rms}}^2 = \frac{1}{N} \; 4\pi N \Big(\frac{m}{2\pi kT}\Big)^{3/2} \int_0^\infty v^4 \mathrm{e}^{-mv^2/2kT} \; \mathrm{d}v$$

$$= 4\pi \Big(\frac{m}{2\pi kT}\Big)^{3/2} \; \frac{3}{8} \Big(\frac{2kT}{m}\Big)^2 \sqrt{\frac{2\pi kT}{m}} = \frac{3kT}{m}$$

Thus, we have

$$v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m}} = 1.732 \sqrt{\frac{kT}{m}}$$

It shows that for an ideal Maxwell-Boltzmann gas, we have

$$v_p \; < \; \overline{v} \; < \; v_{\mathrm{rms}}$$

3. Thermodynamical quantities

For the Maxwell-Boltzmann distribution, we can calculate various thermodynamical quantities as the following.

3.1 Total internal energy

For the Maxwell-Boltzmann energy distribution law, total internal energy of the gas is

$$U = \int_0^\infty En(E)\ \mathrm{d}E$$

Using equation (7.4), we have

$$U = \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^\infty E^{3/2} \mathrm{e}^{-E/kT}\ \mathrm{d}E$$

$$= \frac{2\pi N}{(\pi kT)^{3/2}} \frac{3\sqrt{\pi}(kT)^{5/2}}{4} = \frac{3}{2}\ NkT \tag{7.14}$$

Thus, average internal energy per particle is $3kT/2$.

3.2 Specific heat at constant volume

Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = \frac{3}{2}\ Nk$$

Here, the specific heat at constant volume is independent of T.

3.3 Entropy of the Maxwell-Boltzmann gas

Entropy S of an ideal gas is

$$S = k\ \ln\ W \tag{7.15}$$

Using

$$W = N! \prod_{i=1}^{l} \left[\frac{g_i^{n_i}}{n_i!}\right]$$

we get

$$\ln\ W = \ln\ N! + \sum_{i=1}^{l} (n_i\ \ln\ g_i - \ln\ n_i!$$

Using Stirling formula, we have

$$\ln W = N \ln N - N + \sum_{i=1}^{l} (n_i \ln g_i - n_i \ln n_i + n_i)$$

$$= N \ln N - \sum_{i=1}^{l} n_i \ln \left(\frac{n_i}{g_i}\right) \tag{7.16}$$

and for the maximum value of W, we have

$$n_i = g_i \frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} \mathrm{e}^{-E/kT} \tag{7.17}$$

Using equation (7.17) in (7.16), we have

$$\ln W = N \ln N - \sum_{i=1}^{l} n_i \left(\ln N + \ln\Big[\frac{1}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2}\Big] - \frac{E}{kT}\right)$$

$$= N \ln N - N \ln N - N \ln\Big[\frac{1}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2}\Big] + \frac{EN}{kT}$$

$$= N \ln\Big[V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{EN}{kT}$$

Using $E = 3kT/2$, we have

$$\ln W = N \ln\Big[V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{3}{2} N \tag{7.18}$$

Thus, the entropy (equation 7.18) is

$$S = kN \ln\Big[V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{3}{2} kN \tag{7.19}$$

3.4 Gibbs paradox

In order to check the additive property of entropy of the gas, let us increase each of the volume V and number of particles N of the gas by a common factor p, then the entropy S' of the new system (using equation 7.19) is

$$S' = kpN \ln\Big[pV\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{3}{2} kpN$$

$$= p\Big(kN \ln\Big[V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{3}{2} kN\Big) + pNk \ln(p) \tag{7.20}$$

Using equation (7.19) in (7.20), we get

$$S' = pS + pNk \ln(p)$$

In the new system, particle density $(pN)/(pV) = N/V$ and the energy per particle $(pE)/(pN) = E/N$ remain the same as in the old one. Following the additive property of entropy of the gas, the entropy of the new system should be pS. It shows that the entropy given by equation (7.19) does not satisfy the additive property. This is known as the Gibbs paradox.

Removal of Gibbs paradox

Gibbs paradox can be removed when we introduce a factor $N!$ in the denominator so that entropy S of an ideal gas is

$$S = k \ln\Big(\frac{W}{N!}\Big)$$

Using Stirling formula, we have

$$S = kN \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{5}{2}\, kN \tag{7.21}$$

Now, in order to check additive property of entropy of the gas, let us increase each of the volume V and number of particles N of the gas by a common factor p, then the entropy of the new system is

$$S' = kpN \ln\Big\{\frac{pV}{pN}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big\} + \frac{5}{2}\, pNk$$

$$= p\,\Big[\ln\Big\{\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big\} + \frac{5}{2}\, Nk\Big] = pS$$

Thus, the entropy has the additive property. It shows that the entropy expressed by equation (7.21) is free from any imperfection which leads to the Gibbs paradox.

3.5 Thermodynamical quantities

Accounting for the correction for Gibbs paradox, the partition function Z_N for a system of N particles is

$$Z_N = \frac{Z^N}{N!} = \frac{V^N}{N!}\Big(\frac{2\pi mkT}{h^2}\Big)^{3N/2}$$

(i) Using the Stirling formula, Helmholtz free energy F of the system is

$$F = -kT \ln Z_N = -NkT \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] - NkT$$

Once the Helmholtz free energy of the system is known, we can calculate other thermodynamical quantities of the system.

(ii) Entropy S of the gas is

$$S = -\frac{\partial F}{\partial T} = \frac{5}{2}\, Nk + Nk\, \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big]$$

It is the Sackur-Tetrode equation for entropy of an ideal gas.

(iii) Internal energy U is

$$U = F + ST = \frac{3}{2}\, NkT$$

It is the energy of the ideal gas, showing that the energy per particle is $(3kT/2)$.

(iv) Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = \frac{3}{2}\, Nk$$

Hence, the specific heat at constant volume is independent of T.

4. Ideal Maxwell gas with internal motions

In the preceding section, we considered atomic gas where we have only translational motions. When the gas particles are in the molecular form or we account for internal motions inside a constituent particle, then besides the translational motions, there are internal motions and the energy of each particle is

$$E_j = E_{\rm tr} + E_{\rm in} \qquad \text{where} \qquad E_{\rm tr} = \sum_{i=1}^{3} \frac{p_i^2}{2m}$$

is the energy for the translational motion and $E_{\rm in}$ is the internal energy of the particle. Further, a particle can be in various energy states. The partition function of the gas can be expressed as

$$Z = \frac{1}{N!}\, Z_1^N \tag{7.22}$$

where the factor $N!$ is due to the number of permutations of the particles among themselves and Z_1 the partition function of each particle behaving independently. We have

$$Z_1 = Z_{\rm tr}\, Z_{\rm in} \tag{7.23}$$

where Z_{tr} is the partition function corresponding to the translational motion and is given by (as discussed in the previous section)

$$Z_{\text{tr}} = \frac{1}{h^3}\int \exp\Big(-\frac{E_{\text{tr}}}{kT}\Big)\mathrm{d}p_i\ \mathrm{d}q_i = \frac{1}{h^3}\int \exp\Big(-\sum_{i=1}^{3}\frac{p_i^2}{2mkT}\Big)\mathrm{d}p_i\ \mathrm{d}q_i$$

$$= \frac{1}{h^3}\int \mathrm{d}q_i \prod_{i=1}^{3}\int \exp\Big(-\frac{p_i^2}{2mkT}\Big)\mathrm{d}p_i = V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}$$

and Z_{in} the partition function corresponding to the internal motion which is

$$Z_{\text{in}} = \sum_k g_k\ \mathrm{e}^{-E_k/kT}$$

where the summation runs over various internal states with energies E_k and degeneracies g_k. The Helmholtz free energy F of the system, using equations (7.22) and (7.23), is

$$F = -kT\ \ln Z = -NkT\ \ln Z_1 + kT\ \ln N!$$

$$= -NkT\ \ln(Z_{\text{tr}}\ Z_{\text{in}}) + kT\ \ln N!$$

$$= -NkT\ \ln\Big[V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] - NkT\ \ln Z_{\text{in}} + kT(N\ \ln N - N)$$

$$= -NkT\ \ln\Big[\frac{\mathrm{e}V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] - NkT\ \ln Z_{\text{in}} = F_{\text{tr}} + F_{\text{in}}$$

where

$$F_{\text{tr}} = -NkT\ \ln\Big[\frac{\mathrm{e}V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big]$$

is the Helmholtz free energy for translational motion and

$$F_{\text{in}} = -NkT\ \ln Z_{\text{in}}$$

the Helmholtz free energy due to the internal motion of the particle. Hence, calculation of the Helmholtz free energy of an ideal gas with internal motion requires an explicit expression for Z_{in} based on the knowledge of the internal state of the particle. For accounting for the internal motions of a particle, the internal state is given by (i) the nuclear state, (ii) the electronic state, (iii) the vibrational state and (iv) the rotational state. All of them can be treated as independent of one another and therefore, we can write

$$Z_{\text{in}} = Z_n\ Z_{\text{e}}\ Z_{\text{vib}}\ Z_{\text{rot}}$$

Notice that all the four motions are possible in a molecular gas, whereas in a monoatomic gas, we have internal motion due to electrons and nucleus of the particle.

5. Monoatomic ideal gas with internal motions

For a monoatomic ideal gas, we have translational motion of a particle along with the internal motions due to electrons and nucleus of the particle. For a monoatomic particle we cannot have vibrational and rotational motions. Hence, the energy of each particle is

$$E_j = E_{\text{tr}} + E_n + E_{\text{e}}$$

The partition function of the gas can be expressed as

$$Z = \frac{1}{N!}\, Z_1^N \tag{7.24}$$

where the factor $N!$ is due to the number of permutations of the particles among themselves and Z_1 the partition function of each particle behaving independently

$$Z_1 = Z_{\text{tr}}\; Z_n\; Z_{\text{e}} \tag{7.25}$$

where Z_{tr} is the partition function corresponding to the translational motion and is given by (as discussed earlier)

$$Z_{\text{tr}} = \frac{1}{h^3}\int \exp\Big(-\frac{E_{\text{tr}}}{kT}\Big)\mathrm{d}p_i\; \mathrm{d}q_i = \frac{1}{h^3}\int \exp\Big(-\sum_{i=1}^{3}\frac{p_i^2}{2mkT}\Big)\mathrm{d}p_i\; \mathrm{d}q_i$$

$$= \frac{1}{h^3}\int \mathrm{d}q_i \prod_{i=1}^{3}\int \exp\Big(-\frac{p_i^2}{2mkT}\Big)\mathrm{d}p_i = V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}$$

The Helmholtz free energy F of the system, using equations (7.24) and (7.25), is

$$F = -kT\,\ln Z = -NkT\,\ln Z_1 + kT\,\ln N!$$

$$= -NkT\,\ln(Z_{\text{tr}} Z_n Z_{\text{e}}) + kT\,\ln N!$$

$$= -NkT\,\ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] - NkT - NkT\,\ln Z_n - NkT\,\ln Z_{\text{e}}$$

$$= F_{\text{tr}} + F_n + F_{\text{e}}$$

where

$$F_{\text{tr}} = -NkT\,\ln\Big[\frac{\mathrm{e}V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big]$$

is the Helmholtz free energy for translational motion and

$$F_n = -NkT\ \ln Z_n \qquad \text{and} \qquad F_{\rm e} = -NkT\ \ln Z_{\rm e}$$

the Helmholtz free energies due to the motion of electrons and nucleus, respectively, of the particle.

In case, the temperature is sufficient to excite to the first electronic state with energy E_1 and degeneracy g_1 only, then we have

$$Z_{\rm e} = g_0\ {\rm e}^{-E_0/kT} + g_1\ {\rm e}^{-E_1/kT} = g_0 + g_1\ {\rm e}^{-E_1/kT}$$

where g_0 is the degeneracy and $E_0 = 0$ the energy of the ground state.

For the nuclear spin with quantum number I, it causes the hyperfine splitting of the electronic levels of the atom for the spin quantum number I and the degeneracy is $(2I + 1)$. In the ground (electronic) state if the energy differences between the hyperfine components is small, we can neglect the splitting. Further, we assume that the temperature is not sufficiently high to populate the excited levels or to ionize the particle. Then we have

$$Z_n = (2I + 1)\ {\rm e}^{-E_0/kT} = 2I + 1$$

Now, the Helmholtz free energy is

$$F = -NkT\ \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] - NkT - NkT\ \ln\ \Big(g_0 + g_1\ {\rm e}^{-E_1/kT}\Big)$$

$$-NkT\ \ln(2I + 1)$$

(i) Pressure P of the gas is

$$P = -\frac{\partial F}{\partial V} = \frac{NkT}{V} \qquad \text{or} \qquad PV = NkT = RT$$

where $R = Nk$ is the gas constant. This is the equation of state for an ideal gas.

(ii) Entropy S of the gas is

$$S = -\frac{\partial F}{\partial T} = \frac{5}{2}\ Nk + Nk\ \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big]$$

$$+Nk\ \ln(g_0 + g_1\ {\rm e}^{-E_1/kT}) + \frac{NE_1}{T}\ \frac{g_1\ \exp(-E_1/kT)}{g_0 + g_1\ \exp(-E_1/kT)} + Nk\ \ln(2I + 1)$$

(iii) Internal energy is

$$U = F + ST = -NkT + \frac{5}{2}\ NkT + \frac{NE_1g_1\ \exp(-E_1/kT)}{g_0 + g_1\ \exp(-E_1/kT)}$$

$$= \frac{3}{2}\, NkT + \frac{NE_1 g_1}{g_1 + g_0\, \exp(E_1/kT)}$$

(iv) Specific heat per particle at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = \frac{3}{2}\, Nk + NE_1\, \frac{g_1 g_0\, \exp(E_1/kT)}{[g_1 + g_0\, \exp(E_1/kT)]^2}\, \frac{E_1}{kT^2}$$

$$= \frac{3}{2}\, Nk + \frac{Nk(E_1/kT)^2}{[1 + (g_0/g_1)\exp(E_1/kT)][1 + (g_1/g_0)\exp(-E_1/kT)]}$$

If only ground electronic state is populated, the corresponding expressions can be obtained by putting $g_1 = 0$ in the above expressions.

6. Diatomic ideal gas

For a diatomic ideal gas (gas of diatomic molecules), we have translational motion of a molecule along with the internal motions due to vibration, rotation of the molecule and due to electrons and nuclei of its constituent atoms. Hence, the energy of each particle is

$$E_j = E_{\text{tr}} + E_{\text{vib}} + E_{\text{rot}} + E_n + E_{\text{e}}$$

The partition function of the gas can be expressed as

$$Z = \frac{1}{N!}\, Z_1^N$$

where the factor $N!$ is due to the number of permutations of the particles among themselves and Z_1 the partition function of each particle behaving independently. We have

$$Z_1 = Z_{\text{tr}}\; Z_{\text{vib}}\; Z_{\text{rot}}\; Z_n\; Z_{\text{e}}$$

where Z_{tr} is the partition function corresponding to the translational motion and is given by (as discussed earlier)

$$Z_{\text{tr}} = \frac{1}{h^3} \int \exp\Big(-\frac{E_{\text{tr}}}{kT}\Big) \mathrm{d}p_i\; \mathrm{d}q_i = \frac{1}{h^3} \int \exp\Big(-\sum_{i=1}^{3} \frac{p_i^2}{2mkT}\Big) \mathrm{d}p_i\; \mathrm{d}q_i$$

$$= \frac{1}{h^3} \int \mathrm{d}q_i \prod_{i=1}^{3} \int \exp\Big(-\frac{p_i^2}{2mkT}\Big) \mathrm{d}p_i = V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}$$

The Helmholtz free energy of the system is

$$F = -kT\, \ln Z = -NkT\, \ln Z_1 + kT\, \ln N!$$

$$= -NkT \ln(Z_{\text{tr}} Z_{\text{vib}} Z_{\text{rot}} Z_n Z_{\text{e}}) + kT \ln N!$$

$$= -NkT \ln\Big[V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + kT(N \ln N - N)$$

$$-NkT \ (\ln Z_{\text{vib}} + \ln Z_{\text{rot}} + \ln Z_n + \ln Z_{\text{e}})$$

$$= -NkT \ln\Big[\frac{\text{e}V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] - NkT \ln Z_{\text{vib}} - NkT \ln Z_{\text{rot}}$$

$$-NkT \ln Z_n - NkT \ln Z_{\text{e}}$$

$$= F_{\text{tr}} + F_{\text{vib}} + F_{\text{rot}} + F_n + F_{\text{e}}$$

where

$$F_{\text{tr}} = -NkT \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] - NkT$$

is the Helmholtz free energy for translational motion and

$$F_{\text{vib}} = -NkT \ln Z_{\text{vib}} \qquad F_{\text{rot}} = -NkT \ln Z_{\text{rot}}$$

$$F_n = -NkT \ln Z_n \qquad F_{\text{e}} = -NkT \ln Z_{\text{e}}$$

are Helmholtz free energies due to vibration, rotation of the particle, and the motion of electrons and nuclei of the constituent atoms, respectively. For the given Helmholtz free energy F, we can calculate thermodynamical quantities as follows.

(i) Pressure P of the gas

$$P = -\frac{\partial F}{\partial V} = -\frac{\partial}{\partial V}\Big(F_{\text{tr}} + F_{\text{vib}} + F_{\text{rot}} + F_n + F_{\text{e}}\Big)$$

$$= -\frac{\partial F_{\text{tr}}}{\partial V} - \frac{\partial F_{\text{vib}}}{\partial V} - \frac{\partial F_{\text{rot}}}{\partial V} - \frac{\partial F_n}{\partial V} - \frac{\partial F_{\text{e}}}{\partial V}$$

$$= P_{\text{tr}} + P_{\text{vib}} + P_{\text{rot}} + P_n + P_{\text{e}}$$

(ii) Entropy S of the gas

$$S = -\frac{\partial F}{\partial T} = -\frac{\partial}{\partial T}\Big(F_{\text{tr}} + F_{\text{vib}} + F_{\text{rot}} + F_n + F_{\text{e}}\Big)$$

$$= -\frac{\partial F_{\text{tr}}}{\partial T} - \frac{\partial F_{\text{vib}}}{\partial T} - \frac{\partial F_{\text{rot}}}{\partial T} - \frac{\partial F_n}{\partial V} - \frac{\partial F_{\text{e}}}{\partial T}$$

$$= S_{\text{tr}} + S_{\text{vib}} + S_{\text{rot}} + S_n + S_{\text{e}}$$

(iii) Internal energy U of the gas

$$U = F + ST = (F_{\text{tr}} + F_{\text{vib}} + F_{\text{rot}} + F_n + F_{\text{e}})$$

$$+(S_{\text{tr}} + S_{\text{vib}} + S_{\text{rot}} + S_n + S_{\text{e}})T$$

$$= (F_{\text{tr}} + S_{\text{tr}}T) + (F_{\text{vib}} + S_{\text{vib}}T) + (F_{\text{rot}} + S_{\text{rot}}T)$$

$$+(F_n + S_n\, T) + (F_{\text{e}} + S_{\text{e}}T)$$

$$= U_{\text{tr}} + U_{\text{vib}} + U_{\text{rot}} + U_n + U_{\text{e}}$$

(iv) Specific heat at constant volume c_V

$$c_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}\Big(U_{\text{tr}} + U_{\text{vib}} + U_{\text{rot}} + U_n + U_{\text{e}}\Big)$$

$$= \frac{\partial U_{\text{tr}}}{\partial T} + \frac{\partial U_{\text{vib}}}{\partial T} + \frac{\partial U_{\text{rot}}}{\partial T} + \frac{\partial U_n}{\partial V} + \frac{\partial U_{\text{e}}}{\partial T}$$

$$= c_{\text{tr}} + c_{\text{vib}} + c_{\text{rot}} + c_n + c_{\text{e}}$$

Let us discuss different parts due to various motions, separately.

(A) Translational part

This part is the same as discussed for the monoatomic gas and we have

$$F_{\text{tr}} = -NkT\, \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] - NkT$$

(i) Pressure P_{tr} of the gas is

$$P_{\text{tr}} = -\frac{\partial F_{\text{tr}}}{\partial V} = \frac{NkT}{V} \qquad \text{or} \qquad P_{\text{tr}}V = NkT = RT$$

where $R = Nk$ is the gas constant. This is the equation of state for an ideal gas.

(ii) Entropy $S_{\rm tr}$ of the gas is

$$S_{\rm tr} = -\frac{\partial F_{\rm tr}}{\partial T} = \frac{5}{2}\, Nk + Nk\, \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big]$$

(iii) Internal energy $U_{\rm tr}$ is

$$U_{\rm tr} = F_{\rm tr} + S_{\rm tr}T = \frac{3}{2}\, NkT$$

It is the energy of the ideal gas, showing that the energy per particle is $(3kT/2)$.

(iv) Specific heat $c_{\rm tr}$ at constant volume is

$$c_{\rm tr} = \frac{\partial U_{\rm tr}}{\partial T} = \frac{3}{2}\, Nk$$

Hence, the $c_{\rm tr}$ is independent of T.

(B) Vibrational part

When the temperature is not high, amplitude of the vibrational motion of the atoms in a molecule is not very large and the motion can be considered harmonic with energy

$$E_{\rm vib} = h\nu\Big(v + \frac{1}{2}\Big)$$

where ν is frequency of oscillation, and v the vibrational quantum number, which can assume integer values 0, 1, 2, ... The degeneracy of each vibrational level is unity. The vibrational partition function is

$$Z_{\rm vib} = \sum_{v=0}^{\infty} \exp\Big[-\frac{h\nu}{kT}\Big(v + \frac{1}{2}\Big)\Big] = \exp(-\sigma_v/2) + \exp(-3\sigma_v/2)$$

$$+\exp(-5\sigma_v/2) + \exp(-7\sigma_v/2)\ldots = \frac{\exp(-\sigma_v/2)}{1-\exp(-\sigma_v)}$$

where $\sigma_v = h\nu/kT$. Thus, the Helmholtz free energy is

$$F_{\rm vib} = -NkT\, \ln Z_{\rm vib} = -NkT\, \ln\Big[\frac{\exp(-\sigma_v/2)}{1-\exp(-\sigma_v)}\Big]$$

$$= \frac{1}{2}\, NkT\, \sigma_v + NkT\, \ln\Big[1-\exp(-\sigma_v)\Big]$$

$$= \frac{1}{2}\, Nh\nu + NkT\, \ln\Big[1-\exp\Big(-\frac{h\nu}{kT}\Big)\Big]$$

(i) Entropy S_{vib} of the gas is

$$S_{\text{vib}} = -\frac{\partial F_{\text{vib}}}{\partial T}$$

$$= -Nk \ln\Big[1 - \exp\Big(-\frac{h\nu}{kT}\Big)\Big] + \frac{Nh\nu}{T}\frac{1}{\exp(h\nu/kT) - 1}$$

(ii) Internal energy U_{vib} is

$$U_{\text{vib}} = F_{\text{vib}} + S_{\text{vib}}T = \frac{1}{2}\, Nh\nu + \frac{Nh\nu}{\exp(h\nu/kT) - 1}$$

(iii) Specific heat c_{vib} at constant volume is

$$c_{\text{vib}} = \Big[\frac{\partial U_{\text{vib}}}{\partial T}\Big]_V = kN\Big(\frac{h\nu}{kT}\Big)^2 \frac{\exp(h\nu/kT)}{[\exp(h\nu/kT) - 1]^2}$$

At low temperatures ($kT << h\nu$), we have

$$c_{\text{vib}} = kN\Big(\frac{h\nu}{kT}\Big)^2 \exp(-h\nu/kT)$$

It gives $c_{\text{vib}} \to 0$ as $T \to 0$. At high temperatures ($kT >> h\nu$), we have

$$c_{\text{vib}} = kN\Big(\frac{h\nu}{kT}\Big)^2 \frac{1 + h\nu/kT + (h\nu/kT)^2/2! + \ldots}{(1 + h\nu/kT + (h\nu/kT)^2/2! + \ldots - 1)^2}$$

$$= kN \frac{1 + h\nu/kT + (h\nu/kT)^2/2! + \ldots}{(1 + (h\nu/kT)/2! + (h\nu/kT)^2/3! \ldots)^2}$$

It gives $c_{\text{vib}} \to kN$ as $T \to \infty$. Hence, the contribution due to vibrational motion to the specific heat of a diatomic molecule varies from zero (at $T = 0$) to a maximum value kN at large temperature. Variation of (c_{vib}/Nk) versus $kT/h\nu$ is shown in Figure 3.

(C) Rotational part

For slow rotations, rotational energy of a diatomic molecule can be expressed as

$$E_{\text{rot}} = BJ(J + 1)$$

where B is the rotational constant and J the rotational quantum number which can assume integer values 0, 1, 2, ... The degeneracy of a

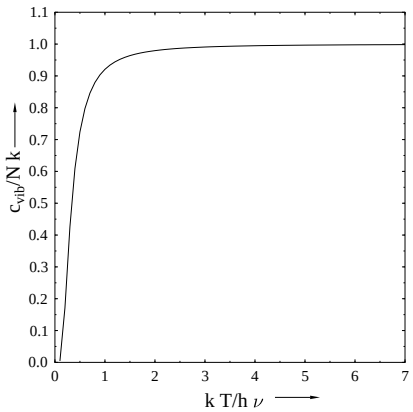

Figure 3: Variation of (c_{vib}/Nk) versus $kT/h\nu$.

rotational level with the quantum number J is $(2J+1)$. The rotational partition function is

$$Z_{\text{rot}} = \sum_{J=0}^{\infty}(2J+1)\,\exp\Big[-\sigma_r J(J+1)\Big]$$

where $\sigma_r = B/kT$.

(i) At low temperatures ($kT << B$, *i.e.*, $\sigma_r >> 1$), we have

$$Z_{\text{rot}} = 1 + \sum_{J=1}^{\infty}(2J+1)\,\exp\Big[-\sigma_r J(J+1)\Big]$$

(a) The Helmholtz free energy is

$$F_{\text{rot}} = -NkT\,\ln Z_{\text{rot}} = -NkT\,\ln[1 + \sum_{J=1}^{\infty}(2J+1)\,\exp\{-\sigma_r J(J+1)\}]$$

$$= -NkT\sum_{J=1}^{\infty}(2J+1)\,\exp[-\sigma_r J(J+1)]$$

where we used the expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3}\ldots$$

and neglected the quadratic and higher order terms.

(b) Entropy S_{rot} of the gas is

$$S_{\text{rot}} = -\frac{\partial F_{\text{rot}}}{\partial T} = Nk\sum_{J=1}^{\infty}(2J+1)\,\exp[-\sigma_r J(J+1)]$$

$$+NkT\sum_{J=1}^{\infty}(2J+1)\,\exp\Big[-\sigma_r J(J+1)\Big]\Big[J(J+1)\Big(\frac{B}{kT^2}\Big)\Big]$$

$$= Nk\sum_{J=1}^{\infty}(2J+1)\,\exp[-\sigma_r J(J+1)]$$

$$+Nk\sum_{J=1}^{\infty}(2J+1)J(J+1)\,\sigma_r\,\exp[-\sigma_r J(J+1)]$$

(c) Internal energy $U_{\rm rot}$ is

$$U_{\rm rot} = F_{\rm rot} + S_{\rm rot}T = NB\sum_{J=1}^{\infty}(2J+1)J(J+1)\,\exp[-\sigma_r J(J+1)]$$

(d) Specific heat $c_{\rm rot}$ at constant volume is

$$c_{\rm rot} = \frac{\partial U_{\rm rot}}{\partial T}$$

$$= NB\sum_{J=1}^{\infty}(2J+1)J(J+1)\,\exp[-\sigma_r J(J+1)]\Big[J(J+1)\frac{B}{kT^2}\Big]$$

$$= kN\Big(\frac{B}{kT}\Big)^2\sum_{J=1}^{\infty}(2J+1)J^2(J+1)^2\,\exp\Big[-\sigma_r J(J+1)\Big]$$

It gives $c_{\rm rot}\to 0$ as $T\to 0$.

(ii) At high temperatures ($kT >> B$, *i.e.*, $\sigma_r << 1$), we have

$$Z_{\rm rot} = \int_{J=0}^{\infty}(2J+1)\,\exp\Big[-\sigma_r J(J+1)\Big]\,{\rm d}J$$

Let $(J^2+J)=u$, hence $(2J+1)\,{\rm d}J = {\rm d}u$, and we have

$$Z_{\rm rot} = \int_{u=0}^{\infty}\exp(-\sigma_r u)\,{\rm d}u = \Big[\frac{\exp(-\sigma_r u)}{-\sigma_r}\Big]_{u=0}^{\infty} = \frac{1}{\sigma_r} = \frac{kT}{B}$$

(a) The Helmholtz free energy is

$$F_{\rm rot} = -NkT\,\ln Z_{\rm rot} = -NkT\,\ln\Big(\frac{kT}{B}\Big)$$

(b) Entropy $S_{\rm rot}$ of the gas is

$$S_{\rm rot} = -\frac{\partial F_{\rm rot}}{\partial T} = Nk\,\ln\Big(\frac{kT}{B}\Big) + Nk$$

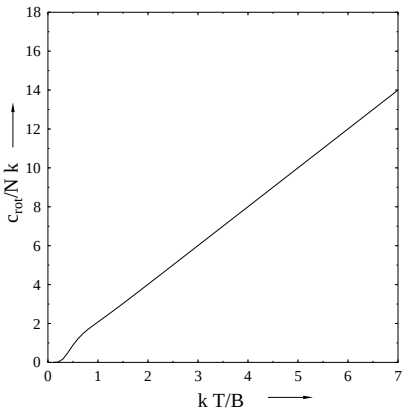

Figure 4: Variation of (c_{rot}/Nk) versus kT/B.

(c) Internal energy U_{rot} is

$$U_{\text{rot}} = F_{\text{rot}} + S_{\text{rot}}T = NkT$$

(d) Specific heat c_{rot} at constant volume is

$$c_{\text{rot}} = \frac{\partial U_{\text{rot}}}{\partial T} = Nk$$

Hence, the specific heat at high temperatures does not depend on T. Variation of (c_{rot}/Nk) versus kT/B is shown in Figure 4.

(D) Effect of nuclear spin

The effect of nuclear spin is important in case of homonuclear diatomic molecules such as the two isotopes of hydrogen atom (H_2 and D_2). In case of heteronuclear diatomic molecules, the effect of nuclear spin is not so important. Let us consider a homonuclear diatomic molecule where each of its constituent atom has spin quantum number i. Hence the resultant spin quantum number I of the molecule can assume the values ranging from 0 to $(2i)$ in steps of unity. For a half integer spin i, total nuclear spin I can be odd or even integers[1], and the relative nuclear partition functions for even and odd values of I are

$$Z'_{\text{even}} = \frac{i}{2i+1} \qquad \text{and} \qquad Z'_{\text{odd}} = \frac{i+1}{2i+1}$$

For an integer spin i, total nuclear spin I can be odd or even integers[2], and the relative nuclear partition functions for even and odd values of I are

[1]For $i = 1/2$, we have $I = 0, 1$

[2]For $i = 1$, we have $I = 0, 1, 2$

$$Z'_{\text{even}} = \frac{i+1}{2i+1} \qquad \text{and} \qquad Z'_{\text{odd}} = \frac{i}{2i+1}$$

Obviously, we have

$$Z'_{\text{even}} + Z'_{\text{odd}} = 1$$

Taking into account the nuclear spin effect, the rotational partition function for such molecules can be modified to

$$Z_{\text{rot}} = 2(Z'_{\text{even}} Z_{\text{even}} + Z'_{\text{odd}} Z_{\text{odd}})$$

where

$$Z_{\text{even}} = \sum_{J=0,2,4,\ldots} (2J+1)\, \exp\Big[-\sigma_r J(J+1)\Big]$$

$$Z_{\text{odd}} = \sum_{J=1,3,5,\ldots} (2J+1)\, \exp\Big[-\sigma_r J(J+1)\Big]$$

The factor 2 appears in the partition function Z_{rot} for rotational motion is divided into two parts Z_{even} and Z_{odd}. At high temperatures, $Z_{\text{even}} \cong Z_{\text{odd}} \cong \frac{1}{2} Z_{\text{rot}} = (kT/2B)$. It shows that at high temperature, the Helmholtz free energy, entropy, internal energy and specific heat of a diatomic molecules does not depend on the nature of the atoms in the molecule. At low temperatures, the situation is different and the gas may be regarded as a combination of two components corresponding to even and odd values of total spin quantum number.

For hydrogen isotopes, the molecules with greater nuclear statistical weight are termed as ortho-hydrogen molecules, whereas those with smaller weight are known as para-hydrogen molecules. Thus, for H_2 and D_2, the nuclear partition functions are as follows:

$$H_2\Big(i = \frac{1}{2}\Big) \begin{cases} \text{ortho} & Z'_{\text{odd}} = \frac{1/2+1}{2} = \frac{3}{4} \\ \text{para} & Z'_{\text{even}} = \frac{1/2}{2} = \frac{1}{4} \end{cases}$$

$$D_2\Big(i = 1\Big) \begin{cases} \text{ortho} & Z'_{\text{even}} = \frac{1+1}{2.1+1} = \frac{2}{3} \\ \text{para} & Z'_{\text{odd}} = \frac{1}{2.1+1} = \frac{1}{3} \end{cases}$$

The relative abundances of the two species in equilibrium are determined by the relative magnitude of the two parts of the partition function Z_{rot}. Thus, the ortho-para ratio is given by

$$\frac{N(\text{ortho-}H_2)}{N(\text{para-}H_2)} = \frac{Z'_{\text{odd}} Z_{\text{odd}}}{Z'_{\text{even}} Z_{\text{even}}} = \frac{3Z_{\text{odd}}}{Z_{\text{even}}}$$

$$\frac{N(\text{ortho-D}_2)}{N(\text{para-D}_2)} = \frac{Z'_{\text{even}} Z_{\text{even}}}{Z'_{\text{odd}} Z_{\text{odd}}} = \frac{2Z_{\text{even}}}{Z_{\text{odd}}}$$

As $T \to 0$, all the molecules tend to be in the lowest rotational state with $J = 0$, and thus the H_2 gas is only para whereas the D_2 gas is only ortho. At high temperatures, $Z_{\text{even}} \cong Z_{\text{odd}}$, the abundance ratio for H_2 is three and for D_2 is two. Hence, as the temperature varies from zero to infinite, the ratio varies from zero to three for H_2 and from zero to two for D_2. However, for all practical purposes, we use the ratio 3 and 2, respectively. The densities of the molecules can be expressed as

$$N_{H_2} = \frac{3}{4}\, N_{\text{ortho}} + \frac{1}{4}\, N_{\text{para}} \qquad \text{and} \qquad N_{D_2} = \frac{2}{3}\, N_{\text{ortho}} + \frac{1}{3}\, N_{\text{para}}$$

Accordingly, the specific heat is

$$(c_{\text{rot}})_{H_2} = \frac{3}{4}\, c_{\text{ortho}} + \frac{1}{4}\, c_{\text{para}} \quad \text{and} \quad (c_{\text{rot}})_{D_2} = \frac{2}{3}\, c_{\text{ortho}} + \frac{1}{3}\, c_{\text{para}}$$

(E) Electronic part

In case, the temperature is sufficient to excite to the first electronic state only with energy E_1 and degeneracy g_1, then we have

$$Z_{\text{e}} = g_0\, \text{e}^{-E_0/kT} + g_1\, \text{e}^{-E_1/kT} = g_0 + g_1\, \text{e}^{-E_1/kT}$$

where g_0 is the degeneracy and $E_0 = 0$ the energy of the ground state.

(a) Free energy is

$$F_{\text{e}} = -NkT\, \ln Z_{\text{e}} = -NkT\, \ln\Big(g_0 + g_1\, \text{e}^{-E_1/kT}\Big)$$

(b) Entropy S_{e} of the gas is

$$S_{\text{e}} = -\frac{\partial F_{\text{e}}}{\partial T}$$

$$= Nk\, \ln\Big(g_0 + g_1\, \text{e}^{-E_1/kT}\Big) + \frac{NE_1}{T}\, \frac{g_1\, \exp(-E_1/kT)}{g_0 + g_1\, \exp(-E_1/kT)}$$

(c) Internal energy U_{e} is

$$U_{\text{e}} = F_{\text{e}} + S_{\text{e}} T = \frac{NE_1 g_1}{g_1 + g_0\, \exp(E_1/kT)}$$

(d) Specific heat c_{e} at constant volume is

$$c_{\text{e}} = \frac{\partial U_{\text{e}}}{\partial T} = NE_1\, \frac{g_1\, g_0\, \exp(E_1/kT)}{[g_1 + g_0\, \exp(E_1/kT)]^2}\, \frac{E_1}{kT^2}$$

$$= \frac{Nk(E_1/k\ T)^2}{[1+(g_0/g_1)\exp(E_1/kT)][1+(g_1/g_0)\exp(-E_1/kT)]}$$

$c_{\rm e} \to 0$ when $T \to 0$ and when $T \to \infty$. If only ground electronic state is populated, *i.e.,* the first excited also is not populated, the expressions can be obtained by putting $g_1 = 0$ in the above expressions.

7. Ideal paramagnetism

Consider a gas of N identical, non-interacting particles, each having magnetic dipole moment $\vec{\mu}$, contained in a volume V at an equilibrium temperature T. For example, in a gas of electrons, each electron may be treated as a small magnetic dipole. When an external magnetic field $\vec{B}$ is applied to this gas, the dipoles tend to orient themselves along the direction of the field, giving rise to paramagnetism. When the density of particles is not large, the gas may be treated as an ideal Boltzmann gas. Energy E_j of each particle is the sum of the translational component $E_{\rm tr}$ and the component $E_{\rm m}$ due to orientation of the magnetic dipole relative to the direction of $\vec{B}$ and we have

$$E_j = E_{\rm tr} + E_{\rm m}$$

where

$$E_{\rm tr} = \sum_{i=1}^{3} \frac{p_i^2}{2m} \qquad \text{and} \qquad E_{\rm m} = -\ \vec{\mu}\ .\ \vec{B}$$

Following the quantum theory, the magnetic moment of a particle cannot be oriented arbitrarily but it is quantized. A well established relation between the magnetic moment μ of a particle and its angular momentum J is

$$\mu = \frac{geh}{4\pi mc}\ J$$

where

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

is the Lande g-factor. Here, S, L and J are, respectively, spin, orbital and total quantum numbers. Thus, we have

$$E_m = -\ \vec{\mu}\ .\ \vec{B} = -\frac{geh}{4\pi mc}\ \ \vec{J}\ .\ \vec{B} = -m_J\ \frac{geh}{4\pi mc}\ B$$

where $m_J = J\cos(\vec{J}, \vec{B})$ is the magnetic quantum number and it can assume $(2J + 1)$ values, ranging from $-J$ to J with increment by 1. The angle between $\vec{J}$ and $\vec{B}$ is denoted by $(\vec{J}, \vec{B})$. Thus, the partition function is

$$Z_m = \sum \mathrm{e}^{-E_m/kT} = \sum_{m_J=-J}^{J} \mathrm{e}^{m_J\alpha}$$

where $\alpha = gehB/4\pi mckT$. Thus, we have

$$Z_m = \mathrm{e}^{-J\alpha}\Big[1 + \mathrm{e}^{\alpha} + \mathrm{e}^{2\alpha} + \ldots + \mathrm{e}^{2J\alpha}\Big] = \mathrm{e}^{-J\alpha}\Big[\frac{\mathrm{e}^{(2J+1)\alpha} - 1}{\mathrm{e}^{\alpha} - 1}\Big]$$

$$= \frac{\mathrm{e}^{(J+1/2)\alpha} - \mathrm{e}^{-(J+1/2)\alpha}}{\mathrm{e}^{\alpha/2} - \mathrm{e}^{-\alpha/2}} = \frac{\sinh[(J + 1/2)\alpha]}{\sinh(\alpha/2)}$$

The partition function of the gas can be expressed as

$$Z = \frac{1}{N!}\,(Z_1)^N$$

where the factor $N!$ is due to the number of permutations of the particles among themselves and Z_1 the partition function of each particle behaving independently

$$Z_1 = Z_{\mathrm{tr}}\; Z_m$$

where Z_{tr} is the partition function corresponding to the translational motion and is given by (as discussed in the previous section)

$$Z_{\mathrm{tr}} = \frac{1}{h^3}\int \exp\Big(-\frac{E_{\mathrm{tr}}}{kT}\Big)\,\mathrm{d}p_i\,\mathrm{d}q_i = \frac{1}{h^3}\int \exp\Big(-\sum_{i=1}^{3}\frac{p_i^2}{2mkT}\Big)\,\mathrm{d}p_i\,\mathrm{d}q_i$$

$$= \frac{1}{h^3}\int \mathrm{d}q_i \prod_{i=1}^{3}\int \exp\Big(-\frac{p_i^2}{2mkT}\Big)\,\mathrm{d}p_i = V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}$$

The Helmholtz free energy of the system is

$$F = -kT\,\ln Z = -NkT\,\ln Z_1 + kT\,\ln N!$$

$$= -NkT\,\ln(Z_{\mathrm{tr}}\;Z_m) + kT\,\ln N!$$

$$= -NkT\,\ln Z_{\mathrm{tr}} - NkT\,\ln Z_m + kT\,\ln N!$$

Using Stirling formula, and expressions for $Z_{\rm tr}$ and Z_m, we get

$$F = -NkT\,\ln\Big[\frac{eV}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] - NkT\,\ln\Big[\frac{\sinh[(J+1/2)\alpha]}{\sinh(\alpha/2)}\Big]$$
$$= F_{\rm tr} + F_m$$

where Helmholtz free energy due to translational motion $F_{\rm tr}$ is

$$F_{\rm tr} = -NkT\,\ln\Big[\frac{eV}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big]$$

and the Helmholtz free energy due to magnetization F_m is

$$F_m = -NkT\,\ln\Big[\frac{\sinh[(J+1/2)\alpha]}{\sinh(\alpha/2)}\Big]$$

We have discussed about the translational contribution. Let us discuss about the magnetization contribution. We can write as

$$F_m = -NkT\,\ln[\sinh\{(J+1/2)\alpha\}] + NkT\,\ln[\sinh(\alpha/2)]$$

(i) Entropy S_m of the gas is

$$S_m = -\frac{\partial F_m}{\partial T} = Nk\,\ln[\sinh\{(J+1/2)\alpha\}] - Nk\,\ln[\sinh(\alpha/2)]$$
$$-Nk\alpha\Big(J+\frac{1}{2}\Big)\,\coth[(J+1/2)\alpha] + \frac{Nk\alpha}{2}\,\coth[\alpha/2]$$
$$= Nk\,\ln\Big[\frac{\sinh[(J+1/2)\alpha]}{\sinh(\alpha/2)}\Big] - Nk\alpha\,\Big(J+\frac{1}{2}\Big)\,\coth[(J+1/2)\alpha]$$
$$+\frac{Nk\alpha}{2}\,\coth[\alpha/2]$$

(ii) Magnetic moment M of the gas is

$$M = -\frac{\partial F_m}{\partial B} = NkT(J+1/2)\,\frac{\alpha}{B}\,\coth[(J+1/2)\alpha] - \frac{NkT\alpha}{2B}\,\coth[\alpha/2]$$

(iii) Internal energy is

$$U_m = F_m + S_mT = -MB$$

(iv) Specific heat at constant volume c_V is

$$c_m = \frac{\partial U_m}{\partial T} = -kN\alpha^2(J+1/2)^2\,\mathrm{cosech}^2[(J+1/2)\alpha]$$
$$+\frac{kN\alpha^2}{4}\,\mathrm{cosech}^2[\alpha/2]$$

Special case

For a free electron, we have $S = 1/2$, $L = 0$ and $J = 1/2$ and thus $g = 2$, $\alpha = 2\mu_B B/kT$. Therefore, the Helmholtz free energy of electron gas is

$$F_m = -NkT \ln\Big[\frac{\sinh(\alpha)}{\sinh(\alpha/2)}\Big] = -NkT \ln[2\cosh(\alpha/2)]$$

(i) Entropy S_m is

$$S_m = -\frac{\partial F_m}{\partial T} = Nk \ln[2\cosh(\alpha/2)] + NkT \tanh(\alpha/2)\ (-\alpha/2T)$$

$$= Nk \ln[2\cosh(\alpha/2)] - \frac{kN\alpha}{2} \tanh(\alpha/2)$$

(ii) Magnetic moment of the electron gas is

$$M = -\frac{\partial F}{\partial B} = NkT \tanh(\alpha/2)\ \frac{\alpha}{2B} = N\mu_B \tanh(\alpha/2)$$

(iii) Internal energy U_m is

$$U_m = F_m + S_m T = -N\mu_B B \tanh(\alpha/2)$$

(iv) Specific heat at constant volume c_m is

$$c_m = \frac{\partial U_m}{\partial T} = -N\mu_B B \operatorname{sech}^2(\alpha/2)\ \Big(-\frac{\alpha}{2T}\Big) = \frac{kN\alpha^2}{4} \operatorname{sech}^2(\alpha/2)$$

It can be expressed as

$$c_m = kN\alpha^2[\exp(\alpha/2) + \exp(-\alpha/2)]^{-2}$$

(a) At low temperature $kT << \mu_B B$, we have

$$c_{\rm m} = kN\alpha^2 \exp(-\alpha)$$

showing that $c_{\rm m} \to 0$ as $T \to 0$.

(b) At high temperature $kT >> \mu_B B$, we have

$$c_{\rm m} = kN\alpha^2\Big(2\Big\{1 + \frac{1}{2!}\frac{\alpha^2}{4} + \frac{1}{4!}\frac{\alpha^4}{16} + \ldots\Big\}\Big)^{-2} \cong kN\ \frac{\alpha^2}{4} = kN\Big(\frac{\mu_B B}{kT}\Big)^2$$

showing that $c_{\rm m}$ is proportional to T^{-2}. Variation of $c_{\rm m}/kN$ with $kT/\mu_B B$ is shown in Figure 5.

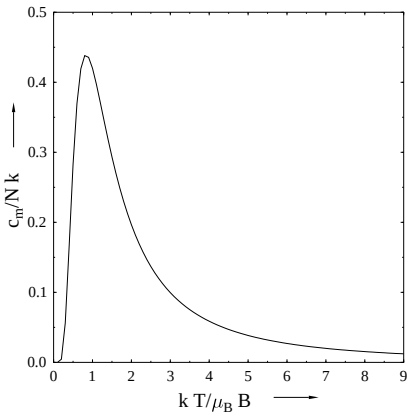

Figure 5: Variation of $(c_{\rm m}/kN)$ versus $kT/\mu_B B$.

Exercise 1. Energy difference between the ground electronic state $^1S_0$ and the first excited state $^3S_1$ of He atom is 159843 cm^{-1}. Calculate the fraction of excited atoms in He gas at 6000 K.

Solution: In a gas in thermal equilibrium at temperature T, the probability $P(i)$ of a gas particles occupying an internal energy level E_i is

$$P(i) = \frac{g_i \ \mathrm{e}^{-E_i/kT}}{\sum_j g_j \ \mathrm{e}^{-E_j/kT}} \qquad \text{Thus,} \qquad P(^3\mathrm{S}_1) = \frac{3 \ \mathrm{e}^{-E_1/kT}}{1 + 3 \ \mathrm{e}^{-E_1/kT}}$$

Using $E_1 = 159843$ cm^{-1}, $T = 6000$ K, we get $\mathrm{e}^{-E_1/kT} = 2.1 \times 10^{-11}$. Thus, we have $P(^3\mathrm{S}_1) = 6.3 \times 10^{-11}$.

8. Problems and questions

1. Define ideal Maxwell-Boltzmann gas and obtain energy distribution function and energy distribution law for it.

2. For an ideal Boltzmann gas, obtain expression for entropy. Discuss the Gibbs paradox and the way for its removal. Obtain expression for chemical potential, Helmholtz free energy and the equation of state for an ideal gas.

3. For an ideal Boltzmann gas, obtain expressions for Helmholtz free energy, entropy, internal energy, specific heat and the equation of state.

4. For Maxwell-Boltzmann energy distribution, obtain expressions for the energy distribution law, average energy, total internal energy and specific heat at constant volume of the gas.

5. Obtain Maxwell-Boltzmann velocity distribution law. Use it to obtain total number of particles, most probable velocity, average velocity, root mean square velocity.

6. For the Maxwell-Boltzmann energy distribution

$$n(E) = \frac{2\pi N}{(\pi kT)^{3/2}}\ E^{1/2}\mathrm{e}^{-E/kT}$$

show that the most probable energy is $E_p = kT/2$ and at this energy the number of particles is

$$n(E_p) = \sqrt{\frac{2}{\pi \mathrm{e}}}\ \frac{N}{kT}$$

7. For the Maxwell-Boltzmann energy distribution

$$n(E) = \frac{2\pi N}{(\pi kT)^{3/2}}\ E^{1/2}\mathrm{e}^{-E/kT}$$

obtain expressions for most probable energy and average energy.

8. For the Maxwell-Boltzmann velocity distribution

$$n(v) = 4\pi N\Big(\frac{m}{2\pi kT}\Big)^{3/2} v^2 \mathrm{e}^{-mv^2/2kT}$$

show that the most probable velocity is $v_p = \sqrt{2kT/m}$ and at this velocity the number of particles is

$$n(v_p) = \frac{4N}{\mathrm{e}}\sqrt{\frac{m}{2\pi kT}}$$

9. For the Maxwell-Boltzmann velocity distribution

$$n(v) = 4\pi N\Big(\frac{m}{2\pi kT}\Big)^{3/2} v^2 \mathrm{e}^{-mv^2/2kT}$$

obtain expressions for most probable velocity, average velocity, root mean square velocity.

10. Derive an expression for entropy for an ideal Maxwell-Boltzmann gas.

11. Derive an expression for specific heat of a diatomic molecule corresponding to its vibrational motion.

12. Derive an expression for specific heat of a diatomic molecule corresponding to its rotational motion and discuss the effect of the nuclear spin for homonuclear diatomic molecule.

13. Derive an expression for specific heat of a diatomic molecule corresponding to its electronic part.

14. Vibrational part of energy of a diatomic molecule is

$$E_{\text{vib}} = h\nu(v + 1/2)$$

where ν is frequency of oscillation, and v the vibrational quantum number. Calculate the corresponding Helmholtz free energy, entropy, internal energy and specific heat at constant volume.

15. Rotational part of energy of a diatomic molecule is

$$E_{\text{rot}} = BJ(J + 1)$$

where B is the rotational constant and J the rotational quantum number. Calculate the corresponding Helmholtz free energy, entropy, internal energy and specific heat at constant volume.

16. Partition function for electronic part of a gas is

$$Z_{\text{e}} = g_0 \text{e}^{-E_0/kT} + g_1 \text{e}^{-E_1/kT} = g_0 + g_1 \text{e}^{-E_1/kT}$$

where g_0 and g_1 are degeneracies, and $E_0 = 0$ and E_1 are energies of ground state and first excited states, respectively. Calculate the corresponding Helmholtz free energy, entropy, internal energy and specific heat at constant volume.

17. Partition function for nuclear part of monoatomic gas is

$$Z_n = 2I + 1$$

where I is the nuclear spin quantum number. Calculate the corresponding Helmholtz free energy, entropy, internal energy and specific heat at constant volume.

18. Derive an expression for thermodynamical quantities for a gas of the particles, having magnetic dipole moments, placed in a magnetic field.

19. Partition function for paramagnetism component is

$$Z_m = \frac{\sinh[(J+1/2)\alpha]}{\sinh(\alpha/2)}$$

where $\alpha = gehB/4\pi mckT$. Calculate the corresponding Helmholtz free energy, entropy, internal energy and specific heat at constant volume.

20. Derive an expression for thermodynamical quantities for a gas of electrons, having magnetic dipole moments, placed in a magnetic field.

21. Write notes on the following

    (i) Maxwell-Boltzmann partition function

    (ii) Limitations of the Maxwell-Boltzmann method

VIII. Fermi-Dirac Gas

Consider a gas consisting of N identical, indistinguishable particles contained in a volume V at an equilibrium temperature T with total energy U. The thermal length $\lambda = h/\sqrt{2\pi mkT}$ of the system is larger than the mean distance between the constituent particles. For such gas of indistinguishable particles, we account for the spin quantum number of the particles, and the gas with a half integer spin quantum number is termed as the Fermi-Dirac gas. For example, spin quantum number of each of the electron, positron, proton, neutron and μ-meson is $1/2$. Total wave function of a system of Fermi-Dirac particles is asymmetric under the exchange of coordinates of any pair of particles, and the particles obey the Pauli exclusion principle, which states that no two particles can occupy a common quantum level. Since we consider that particles in a gas are not interacting with each other, then the gas is known as an ideal Fermi-Dirac gas. Hence, the potential energy of the gas is zero and the total energy of the gas is equal to the sum of the kinetic energies of the constituent particles. The Fermi-Dirac energy distribution is

$$f(E) = \frac{1}{\mathrm{e}^{(\alpha+\beta E)}+1} = \frac{1}{A\ \mathrm{e}^{\beta E}+1}$$

where $\beta = 1/(kT)$ and

$$A = \mathrm{e}^{\alpha} = \mathrm{e}^{-\mu/kT} = \frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}$$

When $A >> 1$, Fermi-Dirac gas reduces to the Maxwell-Boltzmann gas. When A decreases, the gas goes from the maxwellian to Fermi gas. For the Fermi-Dirac gas, $A \leq 1$ and therefore, the chemical potential is positive. Fermi-Dirac gas is said to be weakly degenerate when $A \approx 1$, degenerate when $A < 1$ and strongly degenerate when $A \approx 0$.

1. Weakly degenerate Fermi gas

A gas of low density and high temperature is known as a weakly degenerate gas ($A > 1$). It is the case of rarefied gas. In a Fermi gas, total

number N of particles and total energy U are

$$N = \int_0^\infty f(E)g(E)\ \mathrm{d}E = \int_0^\infty \frac{g(E)}{A\ \mathrm{e}^{\beta E} + 1}\ \mathrm{d}E \tag{8.1}$$

and

$$U = \int_0^\infty Ef(E)g(E)\ \mathrm{d}E = \int_0^\infty \frac{Eg(E)}{A\ \mathrm{e}^{\beta E} + 1}\ \mathrm{d}E \tag{8.2}$$

where

$$g(E)\ \mathrm{d}E = 2g\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\ \mathrm{d}E \tag{8.3}$$

is the number of energy states in the energy range from E to $E + \mathrm{d}E$. Here, g is the degeneracy of the state. For two states of spin, $g = 2$ for an electron. Using equation (8.3) in (8.1) and (8.2), we get

$$N = 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} \int_0^\infty \frac{E^{1/2}}{A\ \mathrm{e}^{\beta E} + 1}\ \mathrm{d}E = 2g\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} F_{3/2}(A) \tag{8.4}$$

and

$$U = 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} \int_0^\infty \frac{E^{3/2}}{A\ \mathrm{e}^{\beta E} + 1}\ \mathrm{d}E = 2g\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} F_{5/2}(A) \tag{8.5}$$

where

$$F_n(A) = \int_0^\infty \frac{E^{n-1}}{A\ \mathrm{e}^{\beta E} + 1}\ \mathrm{d}E$$

Let $\beta E = u$, then $\beta\ \mathrm{d}E = \mathrm{d}u$ and we have

$$F_n(A) = \frac{1}{\beta^n} \int_0^\infty \frac{u^{n-1}}{A\ \mathrm{e}^{u} + 1}\ \mathrm{d}u = (kT)^n \Gamma(n) f_n(A)$$

where

$$f_n(A) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{u^{n-1}}{A\ \mathrm{e}^{u} + 1}\ \mathrm{d}u \tag{8.6}$$

and $\Gamma(n)$ is a gamma function. Thus, equations (8.4) and (8.5) become

$$N = 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} (kT)^{3/2}\ \Gamma(3/2) f_{3/2}(A) = \frac{gV}{\lambda^3}\ f_{3/2}(A) \tag{8.7}$$

and

$$U = 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} (kT)^{5/2}\ \Gamma(5/2) f_{5/2}(A) = \frac{3kTgV}{2\lambda^3}\ f_{5/2}(A) \tag{8.8}$$

where $\lambda = (h^2/2\pi mkT)^{1/2}$ is the thermal wavelength. The ratio U/N is

$$\frac{U}{N} = \frac{3}{2}\, kT\, \frac{f_{5/2}(A)}{f_{3/2}(A)} \qquad \text{or} \qquad U = \frac{3}{2}\, NkT\, \frac{f_{5/2}(A)}{f_{3/2}(A)}$$

When A is large ($A > 1$), we can express

$$\frac{1}{A\ \mathrm{e}^u + 1} = \frac{1}{A\ \mathrm{e}^u}\Big(1 + \frac{1}{A\ \mathrm{e}^u}\Big)^{-1} = \frac{1}{A\ \mathrm{e}^u}\sum_{r=1}^{\infty}(-1)^{r-1}\Big(\frac{1}{A\ \mathrm{e}^u}\Big)^{r-1}$$

$$= \sum_{r=1}^{\infty}(-1)^{r-1}\Big(\frac{1}{A\ \mathrm{e}^u}\Big)^{r}$$

Hence, the integral $f_n(A)$ can be evaluated as the following.

$$f_n(A) = \frac{1}{\Gamma(n)}\int_0^{\infty}\sum_{r=1}^{\infty}(-1)^{r-1}\Big(\frac{1}{A\ \mathrm{e}^u}\Big)^{r} u^{n-1}\ \mathrm{d}u$$

$$= \frac{1}{\Gamma(n)}\sum_{r=1}^{\infty}\frac{(-1)^{r-1}}{A^r}\Big[\int_0^{\infty}\mathrm{e}^{-ru}u^{n-1}\ \mathrm{d}u\Big]$$

Let $ru = x$, then $r\ \mathrm{d}u = \mathrm{d}x$ and we have

$$f_n(A) = \frac{1}{\Gamma(n)}\sum_{r=1}^{\infty}\frac{(-1)^{r-1}}{A^r r^n}\Big[\int_0^{\infty}\mathrm{e}^{-x}x^{n-1}\ \mathrm{d}x\Big] = \sum_{r=1}^{\infty}\frac{(-1)^{r-1}}{A^r r^n}$$

$$= \frac{1}{A} - \frac{1}{A^2 2^n} + \frac{1}{A^3 3^n} - \frac{1}{A^4 4^n} + \dots$$

1.1 Very weakly degenerate gas

A gas with very large value of A is known as very weakly degenerate gas. For that $f_n(A) = A^{-1}$. The gas behaves like a classical gas. For very large values of A, we have

$$\frac{f_{5/2}(A)}{f_{3/2}(A)} = \frac{A^{-1}}{A^{-1}} = 1$$

and total energy

$$U = \frac{3}{2}\, NkT = \frac{3}{2}\, RT$$

where $R = Nk$ is the gas constant. The specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = \frac{3}{2}\, R$$

This expression is the same as for the classical gas.

1.2 Weakly degenerate gas

For $A < 1$, the gas is said to be weakly degenerate and we have

$$f_{5/2}(A) = \frac{1}{A} - \frac{1}{4\sqrt{2}A^2} + \dots$$

and

$$f_{3/2}(A) = \frac{1}{A} - \frac{1}{2\sqrt{2}A^2} + \dots$$

Thus,

$$\frac{f_{5/2}(A)}{f_{3/2}(A)} = \Big(\frac{1}{A} - \frac{1}{4\sqrt{2}A^2} + \dots\Big)\Big(\frac{1}{A} - \frac{1}{2\sqrt{2}A^2} + \dots\Big)^{-1}$$

$$= \frac{1}{A}\Big(1 - \frac{1}{4\sqrt{2}\,A} + \dots\Big)A\Big(1 - \Big[\frac{1}{2\sqrt{2}A} - \dots\Big]\Big)^{-1}$$

$$= \Big(1 - \frac{1}{4\sqrt{2}A} + \dots\Big)\Big(1 + \frac{1}{2\sqrt{2}A} - \dots\Big) = 1 + \frac{1}{4\sqrt{2}}\frac{1}{A} + \dots$$

Putting the value of A in the ratio $f_{5/2}(A)/f_{3/2}(A)$ and using this ratio we get

$$U = \frac{3}{2}\,NkT\Big[1 + \frac{1}{4\sqrt{2}}\frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} + \dots\Big]$$

$$= \frac{3}{2}\,Nk\Big[T + \frac{1}{4\sqrt{2T}}\frac{N}{V}\Big(\frac{h^2}{2\pi mk}\Big)^{3/2} + \dots\Big]$$

Thus, specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = \frac{3}{2}\,kN\Big[1 - \frac{1}{8\sqrt{2T^3}}\frac{N}{V}\Big(\frac{h^2}{2\pi mk}\Big)^{3/2} + \dots\Big]$$

$$= \frac{3}{2}\,kN\Big[1 - \frac{1}{8\sqrt{2}}\frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} - \dots\Big]$$

The first term is the same as for the classical gas, whereas the second term gives the first order correction due to the deviation from the classical behaviour. When the gas is sufficiently rarefied or the temperature is large, the correction terms will be very small. It shows that for deviation from the classical behaviour, the density should be large and/or the temperature should be low. When density and temperature are such that A is of the order of unity, the gas is known as the degenerate one. When $T = 0$, the gas is completely degenerate.

1.3 Fermi-Dirac velocity distribution

The number of energy states in the energy range from E to $E + \mathrm{d}E$ is

$$g(E)\ \mathrm{d}E = 2g\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\ \mathrm{d}E$$

Here, g is the degeneracy. For two spin states, we have $g = 2$ for electron and therefore,

$$g(E)\ \mathrm{d}E = 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\ \mathrm{d}E$$

The number of particles $n(E)\ \mathrm{d}E$ in the energy range from E to $E + \mathrm{d}E$ at $T = 0$ is

$$n(E)\ \mathrm{d}E = f(E)\ g(E)\ \mathrm{d}E = \frac{1}{\mathrm{e}^{(E-E_F)/kT} + 1}\ 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\mathrm{d}E$$

Though the temperature is zero, but the energy levels up to the Fermi level are filled. The energy of Fermi level is denote by E_F. As the temperature T is very low, we can neglect 1 in the denominator of the distribution function to get

$$n(E)\ \mathrm{d}E = \mathrm{e}^{(E_F-E)/kT}\ 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\mathrm{d}E$$

The number of particles $n(v)\ \mathrm{d}v$ in the velocity range from v to $v + \mathrm{d}v$ is

$$n(v)\ \mathrm{d}v = n(E)\ \mathrm{d}E = 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} \mathrm{e}^{E_F/kT}\mathrm{e}^{-E/kT} E^{1/2}\ \mathrm{d}E$$

Using here the relation

$$E = \frac{1}{2}\ mv^2 \qquad \text{so that} \qquad \mathrm{d}E = mv\ \mathrm{d}v$$

we have

$$n(v)\ \mathrm{d}v = \frac{8\pi V m^3 v^2}{h^3}\ \mathrm{e}^{E_F/kT}\ \mathrm{e}^{-mv^2/2kT}\ \mathrm{d}v$$

This is the Fermi-Dirac velocity distribution.

2. Strongly degenerate Fermi gas

The Fermi-Dirac energy distribution is

$$f(E) = \frac{1}{\mathrm{e}^{(E-\mu)/kT} + 1}$$

where μ is the chemical potential which is a function of T, *i.e.*, $\mu = \mu(T)$. Here, α is expressed as $\alpha = -\mu/kT$. At $T = 0$, the gas is strongly degenerate ($A \approx 0$). At $T = 0$, where $\mu = \mu(0) \equiv \mu_0$. The limiting chemical potential μ_0 is known as the Fermi energy E_F of the gas and the distribution function can be written as

$$f(E) = \frac{1}{\mathrm{e}^{(E-E_F)/kT} + 1}$$

2.1 Strongly degenerate Fermi gas at $T = 0$

(i) At $T = 0$, when $E < E_F$, we have

$$f(E) = \frac{1}{\mathrm{e}^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

(ii) At $T = 0$, when $E > E_F$, we have

$$f(E) = \frac{1}{\mathrm{e}^{\infty} + 1} = \frac{1}{\infty + 1} = 0$$

It shows that at $T = 0$, the function $f(E)$ is constant (equal to 1) for the energy up to E_F and then falls to zero suddenly. Thus, at the absolute zero temperature, all the quantum states up to $E = E_F$ are filled and all those above E_F are fully empty. Hence, the Fermi energy can be defined as the energy of the highest level at the absolute zero temperature. Variation of $f(E)$ versus E at $T = 0$ is shown by solid line in Figure 1. The number of energy states in the energy range from E to $E + \mathrm{d}E$ is

$$g(E)\ \mathrm{d}E = 4\pi V \Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\ \mathrm{d}E$$

Here, $g = 2$ is the degeneracy. The number of particles in the energy range from E to $E + \mathrm{d}E$ at $T = 0$ is[1]

$$n(E)\ \mathrm{d}E = f(E)\ g(E)\ \mathrm{d}E = \begin{cases} 4\pi V \Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\ \mathrm{d}E & \text{for } E < E_F \\ 0 & \text{for } E > E_F \end{cases}$$

[1]Using $E = p^2/2m$, the density of states in the energy range from E to $E + \mathrm{d}E$ at $T = 0$ can also be expressed as

$$n(E)\ \mathrm{d}E = 4\pi V \Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2} \mathrm{d}E = \frac{8\pi V p^2}{h^3}\ \mathrm{d}p$$

and therefore we have

$$n(E) = \frac{V 8\pi p^2}{h^3}\ \frac{\mathrm{d}p}{\mathrm{d}E}$$

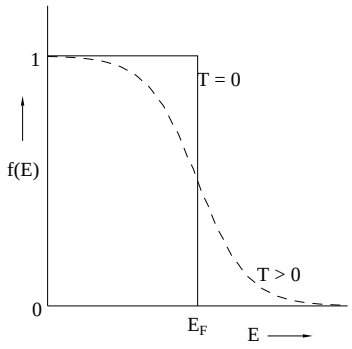

Figure 1: Fermi function $f(E)$ versus E at $T = 0$ (solid line) and $T > 0$ (dotted line)

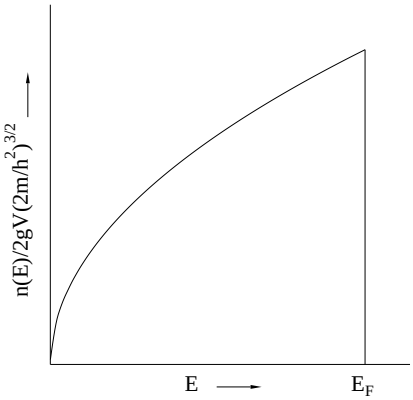

Figure 2: Variation of $n(E)/2gV(2m/h^2)^{3/2}$ versus E at $T = 0$.

Variation of $n(E)/2gV(2m/h^2)^{3/2}$ versus E at $T = 0$ is shown in Figure 2. The total number of particles at $T = 0$ is

$$N = \int_0^{E_F} n(E)\ \mathrm{d}E$$

$$= 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2}\int_0^{E_F} E^{1/2}\ \mathrm{d}E = \frac{8\pi V}{3}\Big(\frac{2m}{h^2}\Big)^{3/2} E_F^{3/2} \tag{8.9}$$

Thus, the Fermi energy is

$$E_F = \Big(\frac{3N}{4\pi gV}\Big)^{2/3}\frac{h^2}{2m}$$

and the Fermi temperature T_F is defined as

$$T_F = \frac{E_F}{k}$$

The Fermi momentum p_F is

$$p_F = (2mE_F)^{1/2} = \Big(\frac{3N}{8\pi V}\Big)^{1/3} h$$

Total energy of the gas at $T = 0$ is

$$U = \int_0^\infty En(E)\ \mathrm{d}E = 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2}\int_0^{E_F} E^{3/2}\mathrm{d}E$$

$$= \frac{8\pi V}{5}\Big(\frac{2m}{h^2}\Big)^{3/2} E_{E_F}^{5/2} = \frac{2g\pi V}{5mh^3}\ p_F^5$$

Thus, at $T = 0$, we have

$$\frac{U}{N} = \frac{3}{5}\ E_F$$

Showing that even at $T = 0$, average energy per particle is 3/5 time the Fermi energy.

(iii) It is also interesting to note that at $T > 0$, when $E = E_F$, we have

$$f(E) = \frac{1}{\mathrm{e}^{0/kT} + 1} = \frac{1}{1+1} = \frac{1}{2}$$

Thus, for $T > 0$, at $E = E_F$, the occupancy is always half.

Exercise 1. Show that for a degenerate Fermi gas, at temperature T, the occupation $f(E)$ at the Fermi level is

$$f(E_F) = \frac{1}{2} + \frac{1}{2}\ \delta_{0T}$$

where δ is the Kronecker delta function.

Solution: The Fermi-Dirac energy distribution is

$$f(E) = \frac{1}{\mathrm{e}^{(E-E_F)/kT} + 1}$$

At $T = 0$, when $E < E_F$, we have

$$f(E) = \frac{1}{\mathrm{e}^{-\infty} + 1} = \frac{1}{0+1} = 1$$

At $T = 0$, when $E > E_F$, we have

$$f(E) = \frac{1}{\mathrm{e}^{\infty} + 1} = \frac{1}{\infty+1} = 0$$

It shows that at $T = 0$, the function $f(E)$ is constant (equal to 1) for the energy up to E_F and then falls to zero suddenly. Thus, at the absolute zero temperature, at $E = E_F$, we have $f(E) = 1$

At $T > 0$, when $E = E_F$, we have

$$f(E) = \frac{1}{e^{0/kT} + 1} = \frac{1}{1+1} = \frac{1}{2}$$

These facts can be combined together as

$$f(E_F) = \frac{1}{2} + \frac{1}{2}\,\delta_{0T}$$

2.2 Strongly degenerate Fermi gas at $T > 0$

At $T > 0$, fraction of levels above E_F are occupied and a fraction of levels below E_F are vacant. The fraction of occupied levels at the energy E is

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$

The fraction of unoccupied levels at the energy E is

$$1 - f(E) = 1 - \frac{1}{e^{(E-E_F)/kT} + 1}$$

$$= \frac{e^{(E-E_F)/kT}}{e^{(E-E_F)/kT} + 1} = \frac{1}{1 + e^{-(E-E_F)/kT}}$$

(i) At $E = E_F + x$, the fraction of occupied levels is

$$f(E_F + x) = \frac{1}{e^{x/kT} + 1}$$

(ii) At $E = E_F - x$, the fraction of unoccupied levels is

$$1 - f(E_F - x) = \frac{1}{1 + e^{x/kT}}$$

It shows that at $T > 0$, the fraction of occupied levels at an energy $E = E_F + x$ is equal to the fraction of unoccupied levels at an energy $E = E_F - x$. Variation of $f(E)$ versus E at $T > 0$ is shown by a dotted line in Figure 1.

Now, we want to study Fermi gas at a finite but low temperature, where $A < 1$. Total number of particles and total energy of the system are

$$N = 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} F_{3/2}(A) \qquad \text{and} \qquad U = 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} F_{5/2}(A)$$

where

$$F_n(A) = \int_0^\infty \frac{E^{n-1}}{\mathrm{e}^{(E-\mu)/kT}+1}\,\mathrm{d}E \tag{8.10}$$

In order to solve integral (8.10) when $A < 1$, let us put $u = (E-\mu)/kT$ then $\mathrm{d}E = kT\,\mathrm{d}u$ and we have

$$F_n(A) = kT\int_{-\mu/kT}^\infty \frac{(\mu+kTu)^{n-1}}{\mathrm{e}^u+1}\,\mathrm{d}u$$

$$= kT\int_{-\mu/kT}^0 \frac{(\mu+kTu)^{n-1}}{\mathrm{e}^u+1}\,\mathrm{d}u + kT\int_0^\infty \frac{(\mu+kTu)^{n-1}}{\mathrm{e}^u+1}\,\mathrm{d}u$$

Changing u by $-u$ in the first integral on the right side, we have

$$F_n(A) = kT\int_0^{\mu/kT} \frac{(\mu-kTu)^{n-1}}{\mathrm{e}^{-u}+1}\,\mathrm{d}u + kT\int_0^\infty \frac{(\mu+kTu)^{n-1}}{\mathrm{e}^u+1}\,\mathrm{d}u$$

Using the relation

$$\frac{1}{\mathrm{e}^{-u}+1} = 1 - \frac{1}{\mathrm{e}^u+1}$$

we get

$$F_n(A) = kT\int_0^{\mu/kT}\Big[1-\frac{1}{\mathrm{e}^u+1}\Big](\mu-kTu)^{n-1}\mathrm{d}u + kT\int_0^\infty\frac{(\mu+kTu)^{n-1}}{\mathrm{e}^u+1}\,\mathrm{d}u$$

$$= kT\int_0^{\mu/kT}(\mu-kTu)^{n-1}\,\mathrm{d}u - kT\int_0^{\mu/kT}\frac{(\mu-kTu)^{n-1}}{\mathrm{e}^u+1}\,\mathrm{d}u$$

$$+kT\int_0^\infty\frac{(\mu+kTu)^{n-1}}{\mathrm{e}^u+1}\,\mathrm{d}u$$

Since $\mu/kT >> 1$, upper limit of the second integral on right side can be taken as infinite. The first integral on right side can be evaluated as the following. Let $(\mu - kTu) = E$, so that $-kT\,\mathrm{d}u = \mathrm{d}E$. Thus, we have

$$kT\int_0^{\mu/kT}(\mu-kTu)^{n-1}\,\mathrm{d}u = -\int_\mu^0 E^{n-1}\,\mathrm{d}E = \int_0^\mu E^{n-1}\,\mathrm{d}E = \frac{\mu^n}{n}$$

Therefore, we have

$$F_n(A) = \frac{\mu^n}{n} - kT\int_0^\infty\frac{(\mu-kTu)^{n-1}}{\mathrm{e}^u+1}\,\mathrm{d}u + kT\int_0^\infty\frac{(\mu+kTu)^{n-1}}{\mathrm{e}^u+1}\,\mathrm{d}u$$

$$= \frac{\mu^n}{n} + kT\mu^{n-1}\int_0^\infty \frac{1}{\mathrm{e}^u+1}\Big[\Big(1+\frac{kTu}{\mu}\Big)^{n-1} - \Big(1-\frac{kTu}{\mu}\Big)^{n-1}\Big]\,\mathrm{d}u$$

$$= \frac{\mu^n}{n} + 2\mu^n\int_0^\infty \frac{\mathrm{d}u}{\mathrm{e}^u+1}\Big[(n-1)\Big(\frac{kT}{\mu}\Big)^2 u + \ldots\Big]$$

$$= \mu^n\Big[\frac{1}{n} + 2(n-1)\Big(\frac{kT}{\mu}\Big)^2\, I + \ldots\Big] \tag{8.11}$$

where the integral I is

$$I = \int_0^\infty \frac{u}{\mathrm{e}^u+1}\,\mathrm{d}u = \int_0^\infty u\,\mathrm{e}^{-u}\Big(1+\mathrm{e}^{-u}\Big)^{-1}\,\mathrm{d}u$$

$$= \int_0^\infty u\,\mathrm{e}^{-u}\Big[1-\mathrm{e}^{-u}+\mathrm{e}^{-2u}-\mathrm{e}^{-3u}+\ldots\Big]\,\mathrm{d}u$$

$$= \int_0^\infty u\Big[\sum_{r=1}^\infty (-1)^{r-1}\mathrm{e}^{-ru}\Big]\,\mathrm{d}u = \sum_{r=1}^\infty (-1)^{r-1}\Big[\int_0^\infty u\,\mathrm{e}^{-ru}\,\mathrm{d}u\Big]$$

Let $ru = x$, then $r\,\mathrm{d}u = \mathrm{d}x$ and we have

$$I = \sum_{r=1}^\infty \frac{(-1)^{r-1}}{r^2}\Big[\int_0^\infty x\,\mathrm{e}^{-x}\mathrm{d}x\Big] = \sum_{r=1}^\infty \frac{(-1)^{r-1}}{r^2}\,\Gamma(2) = \sum_{r=1}^\infty \frac{(-1)^{r-1}}{r^2}$$

Now, we have

$$I = \sum_{r=1}^\infty \frac{(-1)^{r-1}}{r^2} = \frac{\pi^2}{12}$$

Thus, equation (8.11) gives

$$F_n(A) = \frac{\mu^n}{n}\Big[1 + \frac{n(n-1)}{6}\Big(\frac{\pi kT}{\mu}\Big)^2 + \ldots\Big]$$

Hence,

$$F_{3/2}(A) = \frac{2}{3}\,\mu^{3/2}\Big[1 + \frac{1}{8}\Big(\frac{\pi kT}{\mu}\Big)^2 + \ldots\Big] \tag{8.12}$$

and

$$F_{5/2}(A) = \frac{2}{5}\,\mu^{5/2}\Big[1 + \frac{5}{8}\Big(\frac{\pi kT}{\mu}\Big)^2 + \ldots\Big] \tag{8.13}$$

On comparing equations (8.4) and (8.9), we have

$$E_F^{3/2} = \frac{3}{2}\,F_{3/2}(A)$$

Using equation (8.12) in this equation, we have

$$E_F^{3/2} = \mu^{3/2}\Big[1 + \frac{1}{8}\Big(\frac{\pi kT}{\mu}\Big)^2 + \dots\Big]$$

Therefore,

$$\mu = E_F\Big[1 + \frac{1}{8}\Big(\frac{\pi kT}{\mu}\Big)^2 + \dots\Big]^{-2/3} = E_F\Big[1 - \frac{1}{12}\Big(\frac{\pi kT}{\mu}\Big)^2 + \dots\Big]$$

This equation can be solved by the method of iteration, and we can approximate it as

$$\mu \approx E_F\Big[1 - \frac{1}{12}\Big(\frac{\pi T}{T_F}\Big)^2\Big]$$

where $T_F = E_F/k \approx \mu/k$ is the Fermi temperature. Variation of chemical potential of a Fermi gas with T is shown in Figure 3. At $T = 0$, the chemical potential is equal to the Fermi energy E_F. As the temperature increases, the chemical potential decreases, and just below the Fermi temperature, it reduces to zero. With further increase of temperature, the chemical potential becomes more and more negative.

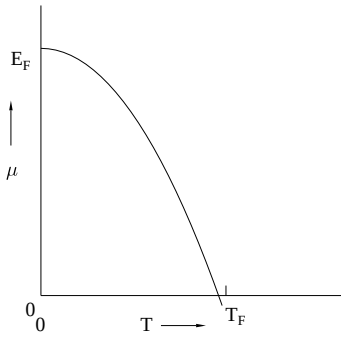

Figure 3: Variation of chemical potential μ with T.

From equations (8.5) and (8.13), we have

$$\begin{aligned} U &= 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} F_{5/2}(A) \\ &= \frac{8}{5}\,\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} \mu^{5/2}\Big[1 + \frac{5}{8}\Big(\frac{\pi kT}{\mu}\Big)^2 + \dots\Big] \end{aligned} \tag{8.14}$$

From equations (8.9) and (8.14), we have

$$\frac{U}{N} = \frac{3}{5}\,\frac{\mu^{5/2}}{E_F^{3/2}}\,\Big[1 + \frac{5}{8}\Big(\frac{\pi kT}{\mu}\Big)^2 + \dots\Big]$$

Using the value of μ, we can approximate

$$\frac{U}{N} = \frac{3}{5}\, E_F\Big[1 - \frac{1}{12}\Big(\frac{\pi T}{T_F}\Big)^2\Big]^{5/2}\Big[1 + \frac{5}{8}\Big(\frac{\pi T}{T_F}\Big)^2\Big]$$

$$= \frac{3}{5}\, E_F\Big[1 - \frac{5}{24}\Big(\frac{\pi T}{T_F}\Big)^2\Big]\Big[1 + \frac{5}{8}\Big(\frac{\pi T}{T_F}\Big)^2\Big]$$

$$= \frac{3}{5}\, E_F\Big[1 + \frac{5}{12}\Big(\frac{\pi T}{T_F}\Big)^2\Big]$$

Thus, we have

$$U \approx \frac{3}{5}\, NE_F\Big[1 + \frac{5}{12}\Big(\frac{\pi T}{T_F}\Big)^2\Big]$$

Hence, the specific heat at constant volume c_V is

$$c_V = \Big[\frac{\partial U}{\partial T}\Big]_V = \frac{\pi^2 N E_F}{2}\, \frac{T}{T_F^2} = \frac{\pi^2 kN}{2}\Big(\frac{T}{T_F}\Big)$$

It shows that c_V varies linearly with T. As $T \to 0$, $c_V \to 0$.

Pressure of the ideal Fermi gas is[2]

$$P = \frac{2U}{3V} = \frac{2NE_F}{5V}\Big[1 + \frac{5}{12}\Big(\frac{\pi T}{T_F}\Big)^2\Big]$$

Helmholtz free-energy of degenerate Fermi gas is

$$F = \mu N - PV$$

$$= NE_F\Big[1 - \frac{1}{12}\Big(\frac{\pi T}{T_F}\Big)^2\Big] - \frac{2}{5}\, NE_F\Big[1 + \frac{5}{12}\Big(\frac{\pi T}{T_F}\Big)^2\Big]$$

$$= NE_F\Big[\frac{3}{5} - \frac{1}{4}\Big(\frac{\pi T}{T_F}\Big)^2\Big]$$

and hence the entropy S of the degenerate Fermi gas is

$$S = -\frac{\partial F}{\partial T} = \frac{NE_F \pi^2 T}{2T_F^2} = \frac{kN\pi^2}{2}\, \frac{T}{T_F}$$

Thus, the entropy S varies linearly with the temperature T.

[2]For an ideal gas, total energy is $U = \frac{3}{2}\, NkT$, and the relation $PV = \frac{2}{3}\, U = NkT = RT$ gives the gas equation with zero potential energy.

3. Thermionic emission

Fermi-Dirac statistics says that at the absolute zero temperature, energy of free electrons moving in a metal varies from zero to the Fermi energy E_F. These electrons having finite value of kinetic energy can move from one place to another within the metal, but are not capable to cross through the metal surface. However, when they are provided sufficient amount of energy by an external source, they can go into the outer space after crossing through the metal surface. The minimum amount of energy required to bring an electron out of the metal surface is known as the work function of the metal. Let it be denoted by ϕ. Hence, for crossing the metal surface, minimum amount of energy of an electron should be $E_F + \phi$. This amount of energy is known as the surface barrier potential energy of the metal and is denoted by E_s

$$E_s = E_F + \phi$$

The work function depends weakly on the temperature. With the increase of temperature, Fermi energy decreases slightly and the work function increases by a small amount. These variations are so small that Fermi energy and work function, for the usual temperatures, can be taken as almost constant. Energy from an external source can be supplied to the metal through a number of ways. For example, it can be imparted by heating the metal (thermionic emission) or by hitting the metal surface by electromagnetic radiations of proper frequencies (photo-electric emission). In the present discussion, we are interested in the thermionic emission where electrons are emitted from the metal surface through the process of heating.

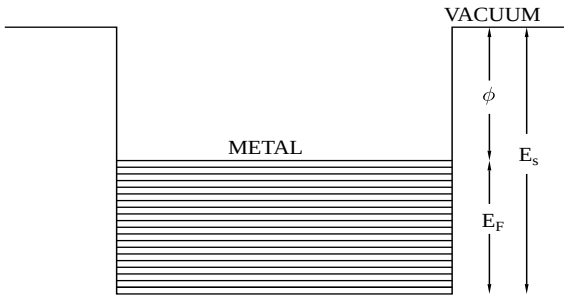

Figure 4: Surface barrier potential.

In order to derive an expression for the thermionic current, let us consider a unit surface area of the metal. Suppose the direction per-

pendicular to the metal surface is denoted by x. Thus, the motions of electrons parallel to the x-direction would be of our interest. Hence, the electrons can escape through the metal surface when their energy satisfies the condition

$$\frac{1}{2}\, mv_x^2 \;\geq\; E_s$$

where v_x is the component of velocity in the x-direction, m the mass of an electron.

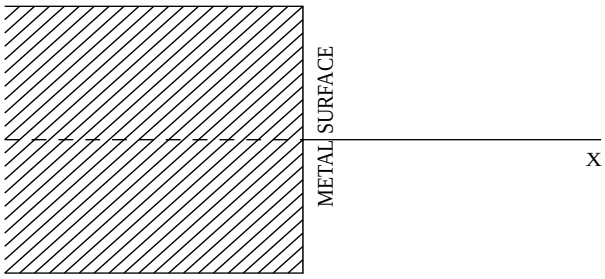

Figure 5: Unit area of a metal surface.

The number of particles $n(v)\ \mathrm{d}v/V$ per unit volume in the velocity range from v to $v + \mathrm{d}v$ is

$$\frac{n(v)\ \mathrm{d}v}{V} = \frac{8\pi m^3 v^2}{h^3}\ \mathrm{e}^{E_F/kT}\mathrm{e}^{-mv^2/2kT}\ \mathrm{d}v$$

If v_x, v_y, v_z be the velocity components of electron in the x, y and z directions, then by writing

$$v^2 = v_x^2 + v_y^2 + v_z^2 \qquad \text{and} \qquad 4\pi v^2\ \mathrm{d}v = \mathrm{d}v_x\ \mathrm{d}v_y\ \mathrm{d}v_z$$

the number of particles per unit volume in the velocity range from v_x to $v_x + \mathrm{d}v_x$, from v_y to $v_y + \mathrm{d}v_y$ and from v_z to $v_z + \mathrm{d}v_z$ is

$$\frac{n(v)\ \mathrm{d}v}{V} = \frac{2m^3}{h^3}\ \mathrm{e}^{E_F/kT}\mathrm{e}^{-m(v_x^2+v_y^2+v_z^2)/2kT}\ \mathrm{d}v_x\ \mathrm{d}v_y\ \mathrm{d}v_z$$

Supposing that the surface of the metal is a plane surface perpendicular to the x-direction, the number of electrons crossing the surface per unit time is

$$n = \frac{2m^3}{h^3}\ \mathrm{e}^{E_F/kT}\int_{\sqrt{2E_s/m}}^{\infty} v_x\ \mathrm{e}^{-mv_x^2/2kT}\mathrm{d}v_x \int_{-\infty}^{\infty}\mathrm{e}^{-mv_y^2/2kT}\mathrm{d}v_y \int_{-\infty}^{\infty}\mathrm{e}^{-mv_z^2/2kT}\mathrm{d}v_z$$

We have

$$\int_{-\infty}^{\infty} \mathrm{e}^{-mv_y^2/2kT}\ \mathrm{d}v_y = \sqrt{\frac{2\pi kT}{m}} \qquad \text{and} \qquad \int_{-\infty}^{\infty} \mathrm{e}^{-mv_z^2/2kT}\ \mathrm{d}v_z = \sqrt{\frac{2\pi kT}{m}}$$

Thus, we have

$$n = \frac{4\pi m^2 kT}{h^3}\ \mathrm{e}^{E_F/kT} \int_{\sqrt{2E_s/m}}^{\infty} v_x\ \mathrm{e}^{-mv_x^2/2kT} \mathrm{d}v_x$$

The current density (*i.e.,* the current per unit surface area) J due to these electrons is

$$J = qn = \frac{4q\pi m^2 kT}{h^3}\ \mathrm{e}^{E_F/kT} \int_{\sqrt{2E_s/m}}^{\infty} v_x\ \mathrm{e}^{-mv_x^2/2kT} \mathrm{d}v_x$$

where q is the charge of an electron. This integral can be solved by putting

$$\frac{1}{2}\frac{mv_x^2}{kT} = y \qquad \text{so that} \qquad v_x\ \mathrm{d}v_x = \frac{kT}{m}\ \mathrm{d}y$$

we get

$$J = \frac{4q\pi mk^2T^2}{h^3}\ \mathrm{e}^{E_F/kT} \int_{E_s/kT}^{\infty} \mathrm{e}^{-y}\ \mathrm{d}y$$

$$= \frac{4q\pi mk^2T^2}{h^3}\ \mathrm{e}^{E_F/kT} \Big[-\mathrm{e}^{-y} \Big]_{E_s/kT}^{\infty} = \frac{4q\pi mk^2T^2}{h^3}\ \mathrm{e}^{E_F/kT}\ \mathrm{e}^{-E_s/kT}$$

$$= \frac{4q\pi mk^2T^2}{h^3}\ \mathrm{e}^{-(E_s - E_F)/kT} = A_0\ T^2\ \mathrm{e}^{-\phi/kT} \tag{8.15}$$

where

$$A_0 = \frac{4q\pi mk^2}{h^3} = \text{a constant} = 1.204\text{x}10^6 \text{A/m}^2\text{K}^2$$

This equation (8.15) is known as the Richardson-Dushmann equation. It is based on the assumption that all the electrons having energy $E \geq E_s$ are escaping out from the metal surface. However, quantum mechanical theory says that an electron having energy $E \geq E_s$ may not necessarily escape from the metal surface and there is some possibility of reflection back into the metal. Suppose r is the reflection coefficient of electron, then the probability of escaping the electron from the metal surface is $(1 - r)$, and the Richardson-Dushmann equation modifies to

$$J = (1 - r) A_0 T^2\ \mathrm{e}^{-\phi/kT}$$

4. Statistical equilibrium in a white dwarf star

A white dwarf is a relatively old star in which most of the hydrogen is converted into helium through thermonuclear reactions. Since the hydrogen is almost exhausted, the material content in the star is the almost helium and the rate of the generation of thermonuclear energy is very slow. Therefore, the luminosity of these stars is very low. Whatever little brightness these stars have, that comes from the gravitational energy release in the process of slow contraction of them. A typical white dwarf is considered to have a mass $M \approx 10^{33}$ g of helium packed in a spherical shape having a density $\rho \approx 10^7$ g/cm^3 with a central temperature $T \approx 10^7$ K. This high value of temperature corresponds to a mean thermal energy of the order of 10^3 eV, which is much larger than the ionization potentials of the helium atom. Thus, practically all the helium there is in the state of complete ionization. The microscopic contents of a white dwarf may be considered as N electrons (each of mass m) and $N/2$ helium nuclei (each of mass $\approx 4m_p$). Thus, the mass of the star is[3]

$$M = Nm + \frac{1}{2}\, N(4m_p) \approx 2Nm_p \tag{8.16}$$

as the mass m_p of proton m_p is much larger than the mass m of electron. The electron density is

$$n = \frac{N}{V} = \frac{M/2m_p}{M/\rho} = \frac{\rho}{2m_p} \approx \frac{10^7}{2 \times 1.6 \times 10^{-24}} \approx 10^{30} \text{ electrons/cm}^3$$

Hence, the Fermi momentum of the electron gas (with $g = 2$) is

$$p_F = \Big(\frac{3N}{8\pi V}\Big)^{1/3} h = \Big(\frac{3n}{8\pi}\Big)^{1/3} h \approx 3 \times 10^{-17} \text{g cm/s}$$

which is comparable with the characteristic momentum $m_0 c$ ($\approx 3 \times 10^{-16}$g cm/s) of an electron. Thus, the Fermi energy E_F of the electron gas would be comparable with the rest mass energy $m_0 c^2$. It shows that (i) the motion of electron in this case is relativistic and (ii) the electron gas is in the (almost) completely degenerate state. The contribution of helium nuclei in comparison to that of the electrons is insignificant and therefore, may be neglected. Further, the contribution of radiation in comparison to that of the electrons can also be neglected. Thus, we are left with the electron gas only. The picture can be further simplified by

[3]In the fusion process in a star, four hydrogen atoms fuse into one helium atom. Here, two electron and two protons form two neutrons. Thus, we fusion process is completed, the number of helium atoms is half of the number of electrons.

assuming a uniform distribution of electrons in the volume of the star and therefore, the spatial variation of various parameters in the problem may be ignored.

Let us now consider the ground-state properties of Fermi gas composed of N relativistic electrons ($g = 2$). The number of electrons $\mathrm{d}N$ in the momentum range from p to $p + \mathrm{d}p$ is

$$\mathrm{d}N = \frac{8\pi V}{h^3}\, p^2\, \mathrm{d}p \tag{8.17}$$

Thus, the total number of electrons is

$$N = \frac{8\pi V}{h^3} \int_0^{p_F} p^2\, \mathrm{d}p = \frac{8\pi V}{3h^3}\, p_F^3 \tag{8.18}$$

Kinetic energy of relativistic electrons is[4]

$$E = m_0 c^2 \Big[\Big\{ 1 + \Big(\frac{p}{m_0 c} \Big)^2 \Big\}^{1/2} - 1 \Big]$$

It shows that the energy E is a function of momentum p. The speed u of electron is[5]

$$u \equiv \frac{\mathrm{d}E}{\mathrm{d}p} = \frac{p}{m_0 [1 + (p/m_0 c)^2]^{1/2}}$$

It shows that the speed u is a function of momentum. Total kinetic energy $\mathrm{d}E_0$ of $\mathrm{d}N$ particles is

$$\mathrm{d}E_0 = E\, \mathrm{d}N = m_0 c^2 \Big[\Big\{ 1 + \Big(\frac{p}{m_0 c} \Big)^2 \Big\}^{1/2} - 1 \Big] \frac{8\pi V}{h^3}\, p^2\, \mathrm{d}p$$

Thus, total kinetic energy of the gas is

$$E_0 = \frac{8\pi V m_0 c^2}{h^3} \int_0^{p_F} \Big[\Big\{ 1 + \Big(\frac{p}{m_0 c} \Big)^2 \Big\}^{1/2} - 1 \Big] p^2\, \mathrm{d}p \tag{8.19}$$

[4]Relativistic energy E' is

$$E'^2 = m_0^2 c^4 + c^2 p^2 \qquad \text{so that} \qquad E' = m_0 c^2 \Big[1 + \Big(\frac{p}{m_0 c} \Big)^2 \Big]^{1/2}$$

Thus, the kinetic energy E is

$$E = E' - m_0 c^2 = m_0 c^2 \Big[\Big\{ 1 + \Big(\frac{p}{m_0 c} \Big)^2 \Big\}^{1/2} - 1 \Big]$$

[5]We have

$$E = \frac{p^2}{2m} \qquad \text{so that} \qquad \frac{\mathrm{d}E}{\mathrm{d}p} = \frac{p}{m} = u$$

The pressure $\mathrm{d}P_0$ of $\mathrm{d}N$ particles is

$$\mathrm{d}P_0 = \frac{pu}{3V}\ \mathrm{d}N = \frac{p}{3V}\ \frac{p}{m_0[1+(p/m_0c)^2]^{1/2}}\ \frac{8\pi V}{h^3}\ p^2\ \mathrm{d}p$$

Thus, total pressure is

$$P_0 = \frac{8\pi}{3h^3}\int_0^{p_F} \frac{p^4}{m_0[1+(p/m_0c)^2]^{1/2}}\ \mathrm{d}p \tag{8.20}$$

On introducing a dimensionless variable θ, defined as

$$p = m_0c\ \sinh theta$$

we get

$$E = m_0c^2(\cosh\theta - 1) \qquad \text{and} \qquad u = c\ \tanh\theta$$

and equations (8.18), (8.19) and (8.20) can be rearranged as

$$N = \frac{8\pi V m_0^3c^3}{3h^3}\ \sinh^3\theta_F = \frac{8\pi V m_0^3c^3}{3h^3}\ x^3$$

and

$$E_0 = \frac{8\pi V m_0^4c^5}{h^3}\int_0^{\theta_F}(\cosh\ \theta - 1)\ \sinh^2\theta\ \cosh\theta\ \mathrm{d}\theta$$

$$= \frac{\pi V m_0^4c^5}{3h^3}\ B(x) \tag{8.21}$$

and

$$P_0 = \frac{8\pi m_0^4c^5}{3h^3}\int_0^{\theta_F}\sinh^4\theta\ \mathrm{d}\theta = \frac{\pi m_0^4c^5}{3h^3}\ A(x) \tag{8.22}$$

where[6]

[6]We have

$$A = 8\int_0^{\theta_F}\sinh^4\theta\ \mathrm{d}\theta = 2\int_0^{\theta_F}(\cosh 2\theta - 1)^2\ \mathrm{d}\theta = 2\int_0^{\theta_F}(\cosh^2 2\theta + 1 - 2\ \cosh 2\theta)\ \mathrm{d}\theta$$

$$= \int_0^{\theta_F}(\cosh 4\theta + 1 + 2 - 4\ \cosh 2\theta)\ \mathrm{d}\theta = \int_0^{\theta_F}(\cosh 4\theta - 4\ \cosh 2\theta + 3)\ \mathrm{d}\theta$$

$$= \frac{\sinh 4\theta_F}{4} - 2\ \sinh 2\theta_F + 3\ \theta_F = \frac{\sinh 2\theta_F\ \cosh 2\theta_F}{2} - 2\ \sinh 2\theta_F + 3\ \theta_F$$

$$= \sinh\theta_F\ \cosh\theta_F\left[1 + 2\ \sinh^2\theta_F - 4\right] + 3\ \theta_F = x\sqrt{1+x^2}\ (2x^2-3) + 3\ \sinh^{-1}x$$

where $x = \sinh\theta_F$.

$$A(x) = 8\int_0^{\theta_F} \sinh^4\theta \ \mathrm{d}\theta = x(x^2+1)^{1/2}\ (2x^2-3) + 3\ \sinh^{-1} x$$

and[7]

$$B(x) = 24\int_0^{\theta_F} (\cosh\theta - 1)\ \sinh^2\theta\ \cosh\theta\ \mathrm{d}\theta$$

$$= 3x(x^2+1)^{1/2}(2x^2+1) - 8x^3 - 3\ \sinh^{-1} x$$

with

$$x = \sinh\theta_F = \frac{p_F}{m_0 c} = \Big(\frac{3n}{8\pi}\Big)^{1/3}\Big(\frac{h}{m_0 c}\Big)$$

The functions $A(x)$ and $B(x)$ can be computed for any required value of x.[8]

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[7] We have

$$B = 24\int_0^{\theta_F} (\cosh\theta - 1)\ \sinh^2\theta\ \cosh\theta\ \mathrm{d}\theta = 24\int_0^{\theta_F} (\cosh^2\theta - \cosh\theta)\ \sinh^2\theta\ \mathrm{d}\theta$$

$$= 24\int_0^{\theta_F} (1 + \sinh^2\theta - \cosh\theta)\ \sinh^2\theta\ \mathrm{d}\theta = 24\int_0^{\theta_F} (1 - \cosh\theta)\ \sinh^2\theta\ \mathrm{d}\theta$$

$$+24\int_0^{\theta_F} \sinh^4\theta\ \mathrm{d}\theta = 12\int_0^{\theta_F} (\cosh 2\theta - 1)\ \mathrm{d}\theta - 24\int_0^{\theta_F} \sinh^2\theta\ \cosh\theta\ \mathrm{d}\theta$$

$$+24\int_0^{\theta_F} \sinh^4\theta\ \mathrm{d}\theta = 6\ \sinh\ 2\theta_F - 12\ \theta_F - 8\ \sinh^3\theta_F + 24\int_0^{\theta_F} \sinh^4\theta\ \mathrm{d}\theta$$

$$= 12\ \sinh\theta_F\ \cosh\theta_F - 12\ \theta_F - 8\ \sinh^2\theta_F + 24\int_0^{\theta_F} \sinh^4\theta\ \mathrm{d}\theta$$

$$= 12x(x^2+1)^{1/2} - 12\ \sinh^{-1} x - 8x^3 + 3[x\sqrt{1+x^2}\ (2x^2-3) + 3\ \sinh^{-1} x]$$

$$= 3x(x^2+1)^{1/2}(2x^2+1) - 8x^3 - 3\ \sinh^{-1} x$$

where $x = \sinh\theta_F$.

[8] The asymptotic results for $x << 1$ and $x >> 1$ are

$$A(x) = \begin{cases} \frac{8}{5}x^5 - \frac{4}{7}x^7 + \frac{1}{3}x^9 - \frac{5}{22}x^{11} + \ldots & \text{for} \quad x << 1 \\ 2x^4 - 2x^2 + 3(\ln 2x - \frac{7}{12}) + (\frac{5}{4}x^{-2}) + \ldots & \text{for} \quad x >> 1 \end{cases}$$

and

$$B(x) = \begin{cases} \frac{12}{5}x^5 - \frac{3}{7}x^7 + \frac{1}{6}x^9 - \frac{15}{176}x^{11} + \ldots & \text{for} \quad x << 1 \\ 6x^4 - 8x^3 + 6x^2 - 3(\ln 2x - \frac{1}{4}) - (\frac{3}{4}x^{-2}) + \ldots & \text{for} \quad x >> 1 \end{cases}$$

In the extreme case when $x \to 0$, the ratio A/B, which is identically equal to the ratio of the pressure p_0 to the energy density E_0/V, tends to a non-relativistic value (2/3). In the opposite case $x \to \infty$, the ratio tends to the extreme relativistic value (1/6).

Let us consider an equilibrium configuration of this model in a crude manner. In absence of the gravitation, it would be necessary to have 'external walls' in order to keep the electron gas at a given density n. The gas will exert a pressure $P_0(n)$ on the walls and any compression or expansion (of the gas) will involve an expenditure of work. Considering the configuration of the star to be spherical, an adiabatic change in the volume V will cause a change $\mathrm{d}E_0$ in the energy of the gas:

$$\mathrm{d}E_0 = -P_0(n)\ \mathrm{d}V = -P_0(R)\ 4\pi R^2 \mathrm{d}R \tag{8.23}$$

In the presence of the gravitation, no external walls are needed, but the change in kinetic energy of gas owing to the change in the size of the sphere would also be given by the equation (8.23). However, equation (8.23) alone cannot provide a net change in energy of the system, as there would be a change in the potential energy also, which is

$$\mathrm{d}E_g = \left(\frac{\mathrm{d}E_g}{\mathrm{d}R}\right)\mathrm{d}R = \alpha\ \frac{GM^2}{R^2}\ \mathrm{d}R$$

where M is the total mass of the gas, G the constant of gravitation and α a number (of the order of unity) whose value depends on the spatial variation of n inside the sphere. In an equilibrium situation, for an infinitesimal change in size, the net change in its energy should be identically zero, and therefore we have

$$\mathrm{d}E_0 + \mathrm{d}E_g = 0 \qquad \text{or} \qquad -P_0(R)\ 4\pi R^2 \mathrm{d}R + \alpha\ \frac{GM^2}{R^2}\ \mathrm{d}R = 0$$

Thus, we have

$$P_0(R) = \frac{\alpha}{4\pi}\ \frac{GM^2}{R^4}$$

Using $P_0(R)$ from equation (8.22) here, we have

$$\frac{\pi m_0^4 c^5}{3h^3} A(x) = \frac{\alpha}{4\pi}\frac{GM^2}{R^4}$$

or

$$A(x) = \frac{3\alpha h^3}{4\pi^2 m_0^4 c^5}\frac{GM^2}{R^4} = \frac{3\alpha}{4\pi^2}\Big(\frac{h/m_0 c}{R}\Big)^3 \frac{GM^2/R}{m_0 c^2} \tag{8.24}$$

where x is

$$x = \Big(\frac{3n}{8\pi}\Big)^{1/3}\frac{h}{m_0 c} = \Big(\frac{9M}{64\pi^2 m_p}\Big)^{1/3}\frac{h/m_0 c}{R}$$

Here, we have used the expression for n. This relation is generally known as the mass-radius relationship for a white dwarf.

It is interesting to look at the combinations of parameters in this equation (8.24): (i) the mass of the star is in terms of the proton mass, (ii) the radius of the star is in terms of the Compton wavelength of the electron and (iii) the gravitational energy of the star is in terms of the rest energy of the electron. It therefore shows a nice combination of quantum mechanics, relativity and gravitation. Here, we cannot express the radius of the star as an explicit function of its mass. However, in two extreme cases, such relation is feasible. Since we have $M \approx 10^{33}$ g, $m_p \approx 10^{-24}$ g and $h/m_0c \approx 10^{-11}$ cm, the argument of the function $A(x)$ in equation (8.24) would be of the order of unity when $R \approx 10^8$ cm. Therefore, we can have two extreme cases as the following:

(i) $R >> 10^8$ cm, so that $x << 1$ and thus we have $A(x) \approx 8x^5/5$ with the result

$$R \approx \frac{3\ (9)^{2/3}}{160\alpha\pi^{4/3}} \frac{h^2 M^{-1/3}}{G m_0 m_p^{5/3}} \propto M^{-1/3} \tag{8.25}$$

(ii) $R << 10^8$ cm, so that $x >> 1$ and thus we have $A(x) \approx 2x^4 - 2x^2$ with the result

$$R \approx \frac{(9)^{1/3}}{4\pi^{2/3}} \frac{h}{m_0 c} \Big(\frac{M}{m_p}\Big)^{1/3} \Big(1 - \Big[\frac{M}{M_0}\Big]^{2/3}\Big)^{1/2} \tag{8.26}$$

where

$$M_0 = \frac{9}{128\pi} \Big(\frac{3}{2\ \alpha^3}\Big)^{1/2} \frac{(hc/G)^{3/2}}{m_p^2} \tag{8.27}$$

It shows that the greater the mass of a white dwarf, the smaller its size. Moreover, there exists a limiting mass M_0 (equation 8.27) that corresponds to a vanishing size of the star. For $M > M_0$, equation (8.26) shows that R cannot be a real number. It can be concluded that all white dwarf stars must have a mass less than M_0. It has been fully supported by the observations. The correct limiting mass of a white dwarf is known as the Chandrasekhar limit. It is 1.44 times the solar mass.

5. Problems and questions

1. Distinguish between weakly degenerate, degenerate and strongly degenerate Fermi gas.

2. Show that for a Fermi-Dirac gas, at $T = 0$, average energy per particle is not zero, but $3E_F/5$, where E_F is the Fermi-energy.

3. Show that for a Fermi-Dirac gas, at $T = 0$, the number of particles $n(E)\ \mathrm{d}E$ in the energy range from E to $E + \mathrm{d}E$ is

$$n(E)\ \mathrm{d}E = \begin{cases} 4\pi V\left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\ \mathrm{d}E & \text{for } E < E_F \\ 0 & \text{for } E > E_F \end{cases}$$

4. Show that for a very weakly degenerate Fermi-Dirac gas, the specific heat at constant volume is

$$c_V = \frac{3}{2}\ kN$$

5. Show that for a weakly degenerate Fermi-Dirac gas, the specific heat at constant volume is

$$c_V = \frac{3}{2}\ kN\Big[1 - \frac{1}{8\sqrt{2}}\frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2} + \ldots\Big]$$

6. Derive an expression for specific heat at constant volume for a weakly degenerate Fermi-Dirac gas. Show that when the density is sufficiently small and/or the temperature is large, the gas behaves like a Maxwell-Boltzmann gas.

7. Show that for a strongly degenerate Fermi gas at $T > 0$, the fraction of occupied levels at energy $E = E_F + x$ is equal to the fraction of unoccupied levels at energy $E = E_F - x$.

8. Show that for a Fermi-Dirac gas, the chemical potential $\mu(T)$ may be expressed as

$$\mu \approx E_F\Big[1 - \frac{1}{12}\Big(\frac{\pi T}{T_F}\Big)^2\Big]$$

where E_F is the Fermi energy and T_F the Fermi temperature.

9. Derive expressions for total number of particles and total energy of a degenerate Fermi-Dirac gas.

10. Derive the Richardson-Dushmann equation for thermionic emission of electrons from a metal surface.

11. Discuss about the statistical equilibrium of white dwarf stars.

12. Show that mass of a white dwarf star cannot be larger than a limiting mass known as the Chandrasekhar limit.

13. Show that for a white dwarf of radius $>> 10^8$ cm, its volume is inversely proportional to its mass.

14. Write notes on the following

    (i) Thermionic emission of electrons

    (ii) Statistical equilibrium in a white dwarf star

    (iii) Chandrasekhar limit

    (iv) Fermi-Dirac velocity distribution

IX. Bose-Einstein Gas

Consider a gas consisting of N identical, indistinguishable particles contained in a volume V at an equilibrium temperature T with total energy U. The thermal length $\lambda = h/\sqrt{2\pi mkT}$ of the system is larger than the mean distance between the constituent particles. For such gas, we do account for the spin quantum number of the particles, and the gas with an integer spin quantum number is termed as the Bose-Einstein gas. For example, spin quantum number of each of the photon and π-meson is 1; of each of the α-particle, deuteron is 0. Total wave function of the system is symmetric under the exchange of coordinates of any pair of particles, and the particles do not obey the Pauli exclusion principle (*i.e.,* any number of particles can occupy a common quantum state). In case of the BE gas, the situation is quite different as compared to that for the Fermi-Dirac (FD) gas. In case of the FD gas, the lower levels are filled first with preference starting from the ground state. Contrary to this situation, in the BE gas, for the kinetic temperature $T \geq T_B$, where T_B is the BE temperature for the gas, the ground state is completely empty and all the system are in the excited states.

Since we consider that particles in a gas are not interacting with each other, then the gas is known as an ideal Bose-Einstein gas. Hence, the potential energy of the gas is zero, and total energy of the gas is equal to the sum of the kinetic energies of the constituent particles. The Bose-Einstein energy distribution is

$$f(E) = \frac{1}{\mathrm{e}^{(\alpha+\beta E)} - 1} = \frac{1}{A\ \mathrm{e}^{\beta E} - 1}$$

where $\beta = 1/(kT)$ and

$$A = \mathrm{e}^{\alpha} = \mathrm{e}^{-\mu/kT} = \frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2} \tag{9.1}$$

Here, μ is chemical potential which is in general a function of T. For a Bose-Einstein gas, $A \geq 1$ and therefore, the chemical potential μ is negative. When $A >> 1$, Bose-Einstein gas reduces to the Maxwell-Boltzmann gas. For Bose-Einstein gas, we have $A > 1$ when $T > T_B$

and $A = 1$ when $T \leq T_B$. Here, T_B is known as the Bose temperature. Pressure of the ideal Fermi gas is[1]

$$P = \frac{2}{3}\,\frac{U}{V}$$

and this relation can be used to find out the equation of state of a gas.

1. Bose-Einstein gas at temperature T

In a Bose-Einstein gas, total number N of particles and total energy U are

$$N = \int_0^\infty f(E)g(E)\ \mathrm{d}E \qquad \text{and} \qquad U = \int_0^\infty Ef(E)g(E)\ \mathrm{d}E$$

where Bose-Einstein energy distribution $f(E)$ is

$$f(E) = \frac{1}{A\ \mathrm{e}^{\beta E} - 1}$$

with $\beta = (1/kT)$ and the number of energy states $g(E)\ \mathrm{d}E$ in the energy range from E to $E + \mathrm{d}E$ is

$$g(E)\ \mathrm{d}E = 2g\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\ \mathrm{d}E$$

where g is the degeneracy. For spin-less particles $g = 1$. Using expressions for $f(E)$ and $g(E)$, we have

$$N = 2g\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} \int_0^\infty \frac{E^{1/2}}{A\ \mathrm{e}^{\beta E} - 1}\ \mathrm{d}E$$

and

$$U = 2g\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} \int_0^\infty \frac{E^{3/2}}{A\ \mathrm{e}^{\beta E} - 1}\ \mathrm{d}E$$

Let $\beta E = u$, then $\beta\ \mathrm{d}E = \mathrm{d}u$ and we have

$$N = 2g\pi V\Big(\frac{2mkT}{h^2}\Big)^{3/2} \int_0^\infty \frac{u^{1/2}}{A\ \mathrm{e}^{u} - 1}\ \mathrm{d}u = \frac{gV}{\lambda^3}\ g_{3/2}(A) \tag{9.2}$$

and

$$U = 2g\pi VkT\Big(\frac{2mkT}{h^2}\Big)^{3/2} \int_0^\infty \frac{u^{3/2}}{A\ \mathrm{e}^{u} - 1}\ \mathrm{d}u = \frac{3kTgV}{2\lambda^3}\ g_{5/2}(A) \tag{9.3}$$

[1]For an ideal gas, total energy is $U = \frac{3}{2}NkT$, and the relation $PV = \frac{2}{3}U = NkT = RT$ gives the gas equation with zero potential energy.

where $\lambda = h/\sqrt{2\pi mkT}$ is thermal length of the system and

$$g_n(A) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{u^{n-1}}{A\ \mathrm{e}^u - 1}\ \mathrm{d}u$$

Here, $\Gamma(n)$ is a gamma function. When A is large ($A > 1$), we can express

$$\frac{1}{A\ \mathrm{e}^u - 1} = \frac{1}{A\ \mathrm{e}^u}\Big(1 - \frac{1}{A\ \mathrm{e}^u}\Big)^{-1} = \frac{1}{A\ \mathrm{e}^u} \sum_{r=1}^{\infty} \Big(\frac{1}{A\ \mathrm{e}^u}\Big)^{r-1} = \sum_{r=1}^{\infty} \Big(\frac{1}{A\ \mathrm{e}^u}\Big)^{r}$$

Hence, the integral $g_n(A)$ can be evaluated as follows

$$g_n(A) = \frac{1}{\Gamma(n)} \int_0^\infty \sum_{r=1}^{\infty} \Big(\frac{1}{A\ \mathrm{e}^u}\Big)^{r} u^{n-1} \mathrm{d}u = \frac{1}{\Gamma(n)} \sum_{r=1}^{\infty} \frac{1}{A^r} \Big[\int_0^\infty \mathrm{e}^{-ru} u^{n-1} \mathrm{d}u\Big]$$

Let $ru = x$, then $r\ \mathrm{d}u = \mathrm{d}x$ and we have

$$g_n(A) = \frac{1}{\Gamma(n)} \sum_{r=1}^{\infty} \frac{1}{A^r} \frac{1}{r^n} \Big[\int_0^\infty \mathrm{e}^{-x} x^{n-1}\ \mathrm{d}x\Big] = \sum_{r=1}^{\infty} \frac{1}{A^r} \frac{1}{r^n} \tag{9.4}$$

Using the values of $g_{3/2}(A)$ in equation (9.2) and of $g_{5/2}(A)$ in (9.3), we get

$$N = \frac{gV}{\lambda^3} \sum_{r=1}^{\infty} \frac{1}{A^r} \frac{1}{r^{3/2}} \tag{9.5}$$

and

$$U = \frac{3kTgV}{2\lambda^3} \sum_{r=1}^{\infty} \frac{1}{A^r} \frac{1}{r^{5/2}} \tag{9.6}$$

2. Bose-Einstein gas at $T \geq T_B$

At a high temperature, most of the particles in a gas are in the excited states. The number of particles in the ground state (with energy $E = 0$) are negligibly small. For high temperature A is quite larger than 1 and in equations (9.5) and (9.6), we can consider two terms and neglect other terms, so that

$$N = \frac{gV}{\lambda^3}\Big[\frac{1}{A} + \frac{1}{A^2 2\sqrt{2}}\Big] \qquad \text{and} \qquad U = \frac{3kTgV}{2\lambda^3}\Big[\frac{1}{A} + \frac{1}{A^2 4\sqrt{2}}\Big]$$

Thus, we have

$$\frac{U}{N} = \frac{3kT}{2}\Big[\frac{1}{A} + \frac{1}{A^2 4\sqrt{2}}\Big]\Big[\frac{1}{A} + \frac{1}{A^2 2\sqrt{2}}\Big]^{-1}$$

$$= \frac{3kT}{2}\Big[1+\frac{1}{A4\sqrt{2}}\Big]\Big[1+\frac{1}{A2\sqrt{2}}\Big]^{-1}$$

$$= \frac{3kT}{2}\Big[1+\frac{1}{A4\sqrt{2}}\Big]\Big[1-\frac{1}{A2\sqrt{2}}\Big]$$

$$= \frac{3kT}{2}\Big[1-\frac{1}{A4\sqrt{2}}\Big] = \frac{3kT}{2}\Big[1-\frac{N}{4\sqrt{2}V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2}\Big]$$

Here, the first term gives the energy for the Boltzmann gas, and the second term gives the first order correction. Thus, we have

$$U = \frac{3}{2}\,Nk\Big[T-\frac{1}{4\sqrt{2\,T}}\frac{N}{V}\Big(\frac{h^2}{2\pi mk}\Big)^{3/2}\Big] \tag{9.7}$$

(i) Specific heat

Specific heat at constant volume c_V is

$$c_V = \Big[\frac{\partial U}{\partial T}\Big]_V = \frac{3}{2}\,kN\Big[1+\frac{1}{8\sqrt{2}}\frac{N}{V}\Big(\frac{h^2}{2\pi mkT}\Big)^{3/2}\Big]$$

The first term is the same as for the classical gas, whereas the second term gives the first order correction due to the deviation from the classical behaviour. When the gas is sufficiently rarefied or the temperature is large, the correction terms will be very small. It shows that for deviation from the classical behaviour density should be large and/or the temperature should be low.

(ii) Pressure

Pressure is

$$P = \frac{2}{3}\,\frac{U}{V}$$

Using equation (9.7) here, we have

$$P = \frac{Nk}{V}\Big[T-\frac{1}{4\sqrt{2T}}\,\frac{N}{V}\Big(\frac{h^2}{2\pi mk}\Big)^{3/2}\Big]$$

or

$$PV = RT\Big[1-\frac{1}{4\sqrt{2}T^{3/2}}\frac{N}{V}\Big(\frac{h^2}{2\pi mk}\Big)^{3/2}\Big]$$

where $R = Nk$. This is the equation of state.

3. Bose-Einstein gas at $T < T_B$

When $T < T_B$, we have $A = 1$. Let N_0 be the number of particles in the ground state and N_e the number in the excited states, so that the total number of particles $N = N_0 + N_e$. At a normal temperature $T > T_B$, all the particles are in the excited states and we have $N = N_e$. Let us consider the spin-less particles, so that $g = 1$. The value of A is 1 at a critical temperature T_B called the Bose temperature. From equation (9.4), we have

$$g_n(1) = \sum_{r=1}^{\infty} \frac{1}{r^n} \equiv \zeta(n)$$

is the Riemann zeta function. The value of $\zeta(3/2)$ is 2.612 and of $\zeta(5/2)$ is 1.341. The Bose temperature can be determined from equation (9.2) by putting $A = 1$. At this temperature T_B, N is practically equal to N_e, showing that up to the Bose temperature, the number of particles in the ground state is negligible. Hence,

$$N = 2.612V\Big(\frac{2\pi mkT_B}{h^2}\Big)^{3/2} \qquad \text{or} \qquad T_B = \Big(\frac{h^2}{2\pi mk}\Big)\Big(\frac{N}{2.612V}\Big)^{2/3} \tag{9.8}$$

The Bose temperature is the minimum temperature at which all the particles are in the excited states. For all known Bose-Einstein gases, value of Bose temperature is very low. For example for He^4, it is about 3.14 K. Though this value is very low, but for the temperature $T \leq T_B$, a Bose-Einstein gas shows a specific behaviour. The number of particles in the excited states is

$$N_e = 2.612V\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2} \tag{9.9}$$

From equations (9.8) and (9.9), we get the number of particles in the excited states

$$\frac{N_e}{N} = \Big(\frac{T}{T_B}\Big)^{3/2} \qquad \text{or} \qquad N_e = N\Big(\frac{T}{T_B}\Big)^{3/2} \tag{9.10}$$

and the number of particles in the ground state

$$N_0 = N - N_e = N\Big[1 - \Big(\frac{T}{T_B}\Big)^{3/2}\Big]$$

These expressions for N_e and N_0 are applicable for $T \leq T_B$. It shows that a large number of particles accumulate in the ground state when $T < T_B$. This is a famous phenomenon, known as the Bose-Einstein condensation. At $T = 0$, all the particles occupy the ground state, and

at $T = T_B$, all the particles occupy the excited state. For $T > T_B$, the particles occupy higher excited states only.

At $T = T_B$, most of the particles are in the excited state. Using the values of $g_{3/2}(1)$ in equation (9.2) and of $g_{5/2}(1)$ in (9.3), we get

$$N_e = \frac{gV}{\lambda^3} 2.612 \quad \text{and} \quad U = \frac{3kTgV}{2\lambda^3} 1.341$$

Thus, we have

$$\frac{U}{N_e} = \frac{3kT(1.341)}{2(2.612)}$$

or

$$U = \frac{1.5 \times 1.341}{2.612}\ N_e kT = 0.770\ NkT\Big(\frac{T}{T_B}\Big)^{3/2} \tag{9.11}$$

where we used equation (9.10).

(i) Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = 1.925Nk\Big(\frac{T}{T_B}\Big)^{3/2} \tag{9.12}$$

At $T = T_B$, we have $c_V(T_B) = 1.925Nk$.

(ii) Entropy S is

$$S = \int_0^T \frac{c_V}{T}\ \mathrm{d}T = \int_0^T 1.925Nk\ \frac{T^{1/2}}{T_B^{3/2}}\ \mathrm{d}T = 1.283Nk\Big(\frac{T}{T_B}\Big)^{3/2}$$

where we have used equation (9.12).

(iii) Helmholtz free energy F is

$$F = U - ST = 0.770\ \frac{NkT^{5/2}}{T_B^{3/2}} - 1.283\ \frac{NkT^{5/2}}{T_B^{3/2}} = -0.513\ \frac{NkT^{5/2}}{T_B^{3/2}}$$

(iv) Pressure P is

$$P = \frac{2}{3}\frac{U}{V}$$

Using equation (9.11) here, we have the equation of state

$$P = 0.513\ \frac{NkT^{5/2}}{T_B^{3/2}}$$

At $T = T_B$

$$P(T_B) = 0.513\ \frac{NkT_B}{V}$$

4. Planck's radiation law

Distribution of energy in the spectrum of black-body remained unexplained for some time. Wien proposed a radiation formula which could explain the spectrum in the short wavelength region whereas the Rayleigh-Jeans law explained the spectrum in the long wavelength region. Planck in 1900 successfully explained the distribution of energy in the spectrum of a black-body for all the wavelengths. This Planck's radiation law can be derived with the help of the Bose-Einstein distribution law in the following manner.

Let a black-body chamber of volume V at temperature T is filled with photons which are moving freely in all directions in the chamber with the speed of light c. Spin quantum number of a photon is 1. Hence, the photons are Bosons and therefore, they follow the Bose-Einstein distribution law which says that at temperature T the number of Bosons having energies in the range from E to $E+\mathrm{d}E$ is

$$n(E)\mathrm{d}E = f(E)g(E)\ \mathrm{d}E = \frac{g(E)\ \mathrm{d}E}{e^{\alpha}e^{E/kT}-1}$$

where $g(E)\ \mathrm{d}E$ is the number of quantum states having energies in the range from E to $E+\mathrm{d}E$. Now,

$$g(E)\ \mathrm{d}E = 2g\pi V\Big(\frac{2m}{h^2}\Big)^{3/2}E^{1/2}\ \mathrm{d}E$$

where g is the degeneracy for state. The parameter $\alpha = -\mu/kT$, where μ is the chemical potential of the particles. The chemical potential for photons is zero. Now, the number of quantum states lying in the frequency range from ν to $\nu + \mathrm{d}\nu$ is

$$g(\nu)\ \mathrm{d}\nu = \frac{8\pi V\nu^2}{c^3}\ \mathrm{d}\nu$$

Thus, the number of photons having frequencies in the range from ν to $\nu + \mathrm{d}\nu$ is

$$n(\nu)\ \mathrm{d}\nu = f(\nu)g(\nu)\ \mathrm{d}\nu = \frac{1}{\mathrm{e}^{h\nu/kT}-1}\frac{8\pi V\nu^2}{c^3}\ \mathrm{d}\nu$$

Now, the energy per unit volume $E_\nu\ \mathrm{d}\nu$ of the chamber of photons having frequencies in the range from ν to $\nu + \mathrm{d}\nu$ is

$$E_\nu\ \mathrm{d}\nu = h\nu\ \frac{n(\nu)\ \mathrm{d}\nu}{V} = h\nu\ \frac{8\pi\nu^2\ \mathrm{d}\nu}{c^3(e^{h\nu/kT}-1)} = \frac{8\pi h}{c^3}\ \frac{\nu^3\ \mathrm{d}\nu}{(\mathrm{e}^{h\nu/kT}-1)}$$

This is Planck's radiation law in terms of frequency ν. It can be transformed in terms of the wavelength λ as the following.

$$\nu = \frac{c}{\lambda} \qquad \text{so that} \qquad \mathrm{d}\nu = -\frac{c}{\lambda^2}\,\mathrm{d}\lambda$$

Here, the negative sign shows that when the frequency increases the wavelength decreases and vice versa. Using these relations, the energy per unit volume of the chamber of the photons having wavelengths in the range from λ to $\lambda + \mathrm{d}\lambda$ is

$$E_\lambda \mathrm{d}\lambda = \frac{8\pi h}{c^3}\frac{(c/\lambda)^3}{(\mathrm{e}^{hc/\lambda kT}-1)}\frac{c}{\lambda^2}\,\mathrm{d}\lambda = \frac{8\pi hc}{\lambda^5}\,\frac{\mathrm{d}\lambda}{(\mathrm{e}^{hc/\lambda kT}-1)} \qquad (9.13)$$

This is Planck's radiation law in terms of wavelength λ. Now, it can be easily shown that Wien's radiation formula and Rayleigh-Jeans radiation law are the special cases of the Planck's radiation law .

Exercise 1. Show that the chemical potential for photon is zero.

Solution: At constant temperature, photons of various energies are being absorbed and re-emitted continuously by the walls of a chamber such that the total energy of the photons is constant. The amount of total energy of the photons in a chamber depends on the temperature of the chamber. In this process, a high energy photon can be converted into a number of low energy photons and vice versa. Though the total energy of photons remains constant, but total number of photons in the chamber is not necessarily constant. Therefore, the condition

$$\sum_i n_i = N \qquad \text{or} \qquad \sum_i \mathrm{d}n_i = 0$$

where N is the total number of Bosons and n_i the number of Bosons in the state with energy E_i is not applicable in case of the photons. Therefore, the multiplier α used in the derivation of Bose-Einstein distribution law should be zero. It gives $e^\alpha = 1$ and $\mu = 0$. Hence, the chemical potential for the photons is zero.

4.1 Wien's radiation formula

In the short wavelength region,

$$\mathrm{e}^{hc/\lambda kT} >> 1$$

and therefore, 1 in the denominator on the right hand side of Planck's radiation law (equation 9.13) can be neglected, and we have

$$E_\lambda\,\mathrm{d}\lambda = \frac{8\pi hc}{\lambda^5}\frac{\mathrm{d}\lambda}{(\mathrm{e}^{hc/\lambda kT})} = \frac{8\pi hc}{\lambda^5}\,\mathrm{e}^{-hc/\lambda kT}\,\mathrm{d}\lambda = \frac{C_1}{\lambda^5}\,\mathrm{e}^{-C_2/\lambda}\,\mathrm{d}\lambda$$

where $C_1 = 8\pi hc$ and $C_2 = hc/kT$ are constants. This relation is the Wien's radiation formula.

4.2 Rayleigh-Jeans radiation law

In the long wavelength region, $(hc/\lambda kT)$ is small and the exponential term on the right hand side of equation (9.13) can be expanded, and we have

$$E_\lambda \, \mathrm{d}\lambda = \frac{8\pi hc}{\lambda^5} \frac{\mathrm{d}\lambda}{(1 + (hc/\lambda kT) + \ldots - 1)} = \frac{8\pi hc}{\lambda^5} \frac{\lambda kT}{hc} \, \mathrm{d}\lambda = \frac{8\pi kT}{\lambda^4} \, \mathrm{d}\lambda$$

This relation is Rayleigh-Jeans radiation law.

4.3 Wien's displacement law

We have (equation 9.13)

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{\mathrm{e}^{hc/\lambda kT} - 1} = \frac{8\pi k^5 T^5}{h^4 c^4} \frac{y^5}{e^y - 1}$$

where $y = hc/\lambda kT$. On differentiation of E_λ with respect to y, we have

$$\frac{\partial E_\lambda}{\partial y} = \frac{8\pi k^5 T^5}{h^4 c^4} \, \frac{y^4}{\mathrm{e}^y - 1} \Big[5 - \frac{y \, \mathrm{e}^y}{\mathrm{e}^y - 1} \Big]$$

For optimum value of E_λ at $\lambda = \lambda_m$, we have

$$5 - \frac{y \, \mathrm{e}^y}{\mathrm{e}^y - 1} = 0 \qquad \text{or} \qquad 5 - 5 \, \mathrm{e}^{-y} - y = 0$$

This equation is satisfied for $y = 4.965$. Thus, we have

$$\frac{hc}{\lambda_m kT} = 4.965 \qquad \text{or} \qquad \lambda_m T = \frac{hc}{k \; 4.965} = 2.899\text{x}10^{-3} \text{ m K}$$

Here, we have used the values of h, c and k. This is the Wien's displacement law.

4.4 Stefan-Boltzmann law

Total energy per unit volume of the chamber is

$$u = \int_0^\infty E_\lambda \, \mathrm{d}\lambda = \int_0^\infty \frac{8\pi hc}{\lambda^5} \frac{1}{\mathrm{e}^{hc/\lambda kT} - 1} \, \mathrm{d}\lambda$$

Let $\lambda = hc/ykT$, and therefore, $\mathrm{d}\lambda = -hc \, \mathrm{d}y/y^2 kT$ and we have

$$u = \int_\infty^0 \frac{8\pi k^5 T^5 y^5}{h^4 c^4 (\mathrm{e}^y - 1)} \Big(- \frac{hc}{y^2 kT} \Big) \, \mathrm{d}y = \frac{8\pi k^4 T^4}{h^3 c^3} \int_0^\infty \frac{y^3}{(\mathrm{e}^y - 1)} \, \mathrm{d}y$$

Using the value of the definite integral

$$\int_0^\infty \frac{y^3}{(e^y - 1)}\, dy = \frac{\pi^4}{15} \qquad \text{we have} \qquad u = \frac{8\pi k^4 T^4}{h^3 c^3}\, \frac{\pi^4}{15}$$

Now total energy emitted per second per unit surface area of the blackbody is

$$E = \frac{cu}{4} = \frac{c}{4}\, \frac{8\pi k^4 T^4}{h^3 c^3}\, \frac{\pi^4}{15} = \sigma T^4$$

where $\sigma = 2\pi^5 k^4/15h^3c^2 = 5.654$ x 10^{-8} joule/sec m^2 K^4 is known as Stefan constant.

Exercise 2. An evacuated box of volume V is in thermal contact with a bath at temperature T. Show that the pressure exerted on the wall of the box by thermal radiation prevailing in it is equal to one-third of the energy density u of thermal radiation.

Solution: The partition function for a harmonic oscillator with characteristic frequency ν_j is

$$Z_j = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)h\nu_j} = \Big[2\ \sinh(\beta h\nu_j/2)\Big]^{-1}$$

The partition function Z for a system of independent oscillators having various characteristic frequencies is

$$Z = \prod_j Z_j$$

The Helmholtz free energy is

$$F = -kT\ \ln Z = kT \sum_j \ln[2\ \sinh(\beta h\nu_j/2)]$$

The number of quantum states lying in the frequency range from ν to ν + dν is

$$g(\nu)\ d\nu = \frac{8\pi V \nu^2}{c^3}\ d\nu$$

Then the Helmholtz free energy can be expressed as

$$F = kT \int_0^\infty \ln[2\ \sinh(\beta h\nu/2)] g(\nu)\ d\nu$$

The internal energy U is

$$U = -T^2\Big[\frac{\partial(F/T)}{\partial T}\Big] = \int_0^\infty \epsilon(\nu, T) g(\nu)\ d\nu$$

where the mean energy of harmonic oscillators is

$$\epsilon(\nu, T) = \frac{h\nu}{2}\ \coth(\beta h\nu/2) = \frac{h\nu}{2} + \frac{h\nu}{\mathrm{e}^{\beta h\nu} - 1} \tag{9.14}$$

The pressure P is

$$P = -\frac{\partial F}{\partial V} = -kT \int_0^\infty \frac{8\pi\nu^2 \mathrm{d}\nu}{c^3}\ \ln[2\ \sinh(\beta h\nu/2)]$$

Using partial integration, we get

$$P = -kT\frac{8\pi\nu^3 \mathrm{d}\nu}{3c^3}\ \ln\Big[2\ \sinh(\beta h\nu/2)\Big]\Big|_0^\infty + kT\int_0^\infty \frac{8\pi\nu^3 \mathrm{d}\nu}{3c^3}\frac{h}{2kT}\ \coth(\beta h\nu/2)$$

$$= \frac{1}{3}\int_0^\infty \frac{8\pi\nu^2 \mathrm{d}\nu}{c^3}\Big[\frac{h\nu}{2} + \frac{h\nu}{\mathrm{e}^{\beta h\nu} - 1}\Big]$$

Using relation (9.14) here, we get

$$P = \frac{1}{3}\int_0^\infty \frac{8\pi\nu^2 \mathrm{d}\nu}{c^3}\ \epsilon(\nu, T) = \frac{1}{3}\ u$$

where u is the energy density.

5. Debye model of solids (Phonons)

Here, we account for simple mono-atomic solids comprising a large number N of atoms arranged in a regular array, called a lattice. Each atom is a solid and has its position of equilibrium, in the lattice, about which it vibrates due to the thermal agitations. The system may be considered as comprising a large number N of non-interacting, identical, linear harmonic oscillators, each of mass m, in thermal equilibrium at temperature T. In quantum theory, energy of oscillators is quantized and they exchange energy through the quanta, called phonons. There are $3N$ degrees of freedom. Let ω_i be the frequency for the i-th degree of freedom. In quantum mechanics, the energy for the i-th degree of freedom is

$$E_n = \hbar\omega_i\Big(n + \frac{1}{2}\Big)$$

where n can assume integer values 0, 1, 2, 3, ... The corresponding partition function is

$$Z_i = \sum_n \exp\Big(-\frac{E_n}{kT}\Big) == \sum_{n=0}^\infty \exp\Big\{-\frac{\hbar\omega_i}{kT}\Big(n + \frac{1}{2}\Big)\Big\}$$

We know that

$$\sum_{n=0}^{\infty}\exp\Big\{-\frac{\hbar\omega_i}{kT}\Big(n_i+\frac{1}{2}\Big)\Big\}=\exp\Big(-\frac{\hbar\omega_i}{2kT}\Big)+\exp\Big(-\frac{3\hbar\omega_i}{2kT}\Big)+\exp\Big(-\frac{5\hbar\omega_i}{2kT}\Big)$$

$$+\exp\Big(-\frac{7\hbar\omega_i}{2kT}\Big)+\ldots=\frac{\exp(-\hbar\omega_i/2kT)}{1-\exp(-\hbar\omega_i/kT)}$$

Thus, the partition function is

$$Z_N=\prod_{i=1}^{3N}\Big[\frac{\exp(-\hbar\omega_i/2kT)}{1-\exp(-\hbar\omega_i/kT)}\Big] \tag{9.15}$$

The number of modes of vibration in the frequency range from ω to $\omega+\mathrm{d}\omega$ for the three directions of polarization (one longitudinal and two transverse) is[2]

$$g(\omega)\mathrm{d}\omega=\frac{V}{2\pi^2}\Big[\frac{1}{u_l^3}+\frac{2}{u_t^3}\Big]\omega^2\mathrm{d}\omega \tag{9.16}$$

where in general u_l and u_t are not equal. The total number of modes of vibrations in a mono-atomic solid is $3N$. Therefore, in the Debye model, we have

$$3N=\int_0^{\omega_D}g(\omega)\mathrm{d}\omega=\frac{V}{6\pi^2}\Big[\frac{1}{u_l^3}+\frac{2}{u_t^3}\Big]\omega_D^3$$

Hence,

$$\omega_D^3=\frac{18\pi^2N}{V}\Big[\frac{1}{u_l^3}+\frac{2}{u_t^3}\Big]^{-1} \tag{9.17}$$

[2]We know that the number of quantum states lying in the frequency range from ν to $\nu+\mathrm{d}\nu$ is

$$g(\nu)\ \mathrm{d}\nu=\frac{4\pi V\nu^2}{c^3}\ \mathrm{d}\nu$$

or in the frequency range from ω to $\omega+\mathrm{d}\omega$ is

$$g(\omega)\ \mathrm{d}\omega=\frac{4\pi V(\omega/2\pi)^2}{c^3}\ \frac{\mathrm{d}\omega}{2\pi}=\frac{V\omega^2}{2\pi^2c^3}\ \mathrm{d}\omega$$

When the wave propagates with velocity u and there are three directions of polarization, the number of quantum states lying in the frequency range from ω to $\omega+\mathrm{d}\omega$ is

$$g(\omega)\mathrm{d}\omega=\frac{V}{2\pi^2}\Big[\frac{1}{u_l^3}+\frac{2}{u_t^3}\Big]\omega^2\mathrm{d}\omega$$

where one directions of polarization is longitudinal with velocity u_l and two directions of polarization are transverse with with velocity u_t.

where ω_D is the Debye frequency, the highest possible frequency. From equations (9.16) and (9.17) we have

$$g(\omega)\mathrm{d}\omega = \frac{9N}{\omega_D^3}\,\omega^2\mathrm{d}\omega \tag{9.18}$$

(i) Helmholtz Free energy F of the system is

$$F = -kT\,\ln Z_N = -kT\,\ln\Big(\prod_{i=1}^{3N}\Big[\frac{\exp(-\hbar\omega_i/2kT)}{1-\exp(-\hbar\omega_i/kT)}\Big]\Big)$$

$$= -kT\,\sum_{i=1}^{3N}\Big[\ln\Big(\frac{\exp(-\hbar\omega_i/2kT)}{1-\exp(-\hbar\omega_i/kT)}\Big)\Big]$$

$$= \sum_{i=1}^{3N}\Big[\frac{1}{2}\,\hbar\omega_i + kT\,\ln\Big\{1-\exp\Big(-\frac{\hbar\omega_i}{kT}\Big)\Big\}\Big] \tag{9.19}$$

For continuous variation of frequency, we can change the summation into integration as

$$F = \int_0^{\omega_D}\Big[\frac{1}{2}\,\hbar\omega + kT\,\ln\Big\{1-\exp\Big(-\frac{\hbar\omega}{kT}\Big)\Big\}\Big]g(\omega)\,\mathrm{d}\omega$$

Using equation (9.18), we have

$$F = \int_0^{\omega_D}\Big[\frac{1}{2}\,\hbar\omega + kT\,\ln\Big\{1-\exp\Big(-\frac{\hbar\omega}{kT}\Big)\Big\}\Big]\frac{9N}{\omega_D^3}\omega^2\mathrm{d}\omega$$

$$= \frac{9\hbar N}{2\omega_D^3}\int_0^{\omega_D}\omega^3\mathrm{d}\omega + \frac{9NkT}{\omega_D^3}\int_0^{\omega_D}\ln\Big\{1-\exp\Big(-\frac{\hbar\omega}{kT}\Big)\Big\}\omega^2\mathrm{d}\omega$$

$$= NE_0 + \frac{9NkT}{\omega_D^3}\int_0^{\omega_D}\ln\Big\{1-\exp\Big(-\frac{\hbar\omega}{kT}\Big)\Big\}\omega^2\mathrm{d}\omega$$

where $E_0(=9\,\hbar\omega_D/8)$ is the zero-point energy.

(ii) Entropy S of the system is

$$S = -\frac{\partial F}{\partial T} = -\frac{9Nk}{\omega_D^3}\int_0^{\omega_D}\ln\Big\{1-\exp\Big(-\frac{\hbar\omega}{kT}\Big)\Big\}\omega^2\mathrm{d}\omega$$

$$+\frac{9NkT}{\omega_D^3}\int_0^{\omega_D}\frac{\exp(-\hbar\omega/kT)}{\{1-\exp(-\hbar\omega/kT)\}}\frac{\hbar\omega}{kT^2}\omega^2\mathrm{d}\omega$$

$$= -\frac{9Nk}{\omega_D^3}\int_0^{\omega_D} \ln\Big\{1 - \exp\Big(-\frac{\hbar\omega}{kT}\Big)\Big\}\omega^2 \mathrm{d}\omega$$

$$+\frac{9N\hbar}{\omega_D^3 T}\int_0^{\omega_D} \frac{\omega^3}{\exp(\hbar\omega/kT) - 1}\mathrm{d}\omega$$

(iii) Internal energy U is

$$U = F + ST = NE_0 + \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D} \frac{\omega^3}{\exp(\hbar\omega/kT) - 1}\mathrm{d}\omega$$

$$= \frac{9N\hbar\omega_D}{8} + 3NkT\ D(x_0)$$

putting $x = \hbar\omega/kT$, $D(x_0)$ is defined as the Debye function

$$D(x_0) = \frac{3}{x_0^3}\int_0^{x_0} \frac{x^3}{\mathrm{e}^x - 1}\mathrm{d}x$$

with $x_0 = (\hbar\omega_D/kT) = (T_D/T)$. Here, T_D is known as Debye temperature. The Debye function can be evaluated for the limiting temperatures

(a) At high temperature, $x << 1$ and we have

$$D(x_0) = \frac{3}{x_0^3}\int_0^{x_0} x^3\Big[x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots\Big]^{-1}\mathrm{d}x$$

$$= \frac{3}{x_0^3}\int_0^{x_0} x^2\Big[1 - \frac{x}{2} + \frac{x^2}{12} + \ldots\Big]\mathrm{d}x = \frac{3}{x_0^3}\int_0^{x_0}\Big[x^2 - \frac{x^3}{2} + \frac{x^4}{12}\ldots\Big]\mathrm{d}x$$

$$= \frac{3}{x_0^3}\Big[\frac{x_0^3}{3} - \frac{x_0^4}{8} + \frac{x_0^5}{60} + \ldots\Big] = 1 - \frac{3}{8}\ x_0 + \frac{1}{20}\ x_0^2 + \ldots$$

Thus, we have

$$U = NE_0 + 3NkT\Big[1 - \frac{3}{8}\ x_0 + \frac{1}{20}\ x_0^2 + \ldots\Big]$$

$$= NE_0 + 3NkT\Big[1 - \frac{3}{8}\frac{T_D}{T} + \frac{1}{20}\Big(\frac{T_D}{T}\Big)^2 + \ldots\Big]$$

$$= 3NkT\Big[1 + \frac{1}{20}\Big(\frac{T_D}{T}\Big)^2 + \ldots\Big]$$

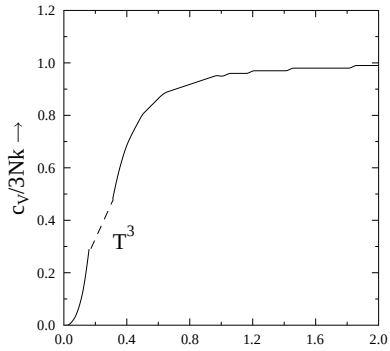


Figure 1. Variation of $c_V/3Nk$ versus T.

Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = 3Nk\Big[1 - \frac{1}{20}\Big(\frac{T_D}{T}\Big)^2\Big]$$

It shows that $c_V \to 3Nk$ as $T \to \infty$.

(b) At low temperature, $x >> 1$ and the upper limit x_0 can be replaced by ∞, and thus,

$$D(x_0) = \frac{3}{x_0^3}\int_0^\infty x^3 \ \mathrm{e}^{-x}\ \mathrm{d}x = \frac{3}{x_0^3}\ \Gamma(4) = 18\Big(\frac{T}{T_D}\Big)^3$$

Thus, we have

$$U = NE_0 + 54NkT\Big(\frac{T}{T_D}\Big)^3$$

Specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = 216Nk\Big(\frac{T}{T_D}\Big)^3$$

It show that $c_V \to 0$ ad $T \to 0$, and in the low temperature region, c_V varies as T^3. Variation of $c_V/3Nk$ versus T is shown in Figure 1.

6. Liquid He^4

Two isotopes, He^3 and He^4, of helium have significantly different properties. The reason for this is that due to their nuclear spins they follow different distribution laws. The He^3 has spin $1/2$ and follows Fermi-Dirac statistics whereas He^4 has spin zero and follows Bose-Einstein statistics.

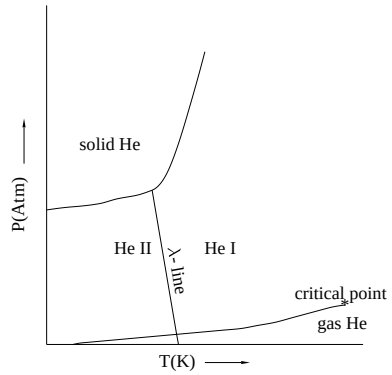


Figure 2: Phase diagram for liquid He^4 (not to the scale).

A remarkable property of both the helium isotopes is that they remain in the liquid form, probably down to the absolute zero temperature.

Phase diagram of He^4 is shown in Figure 2. A peculiar property of He^4 is that it has two liquid phases, called HeI and HeII, and a transition from one phase to other is known as the λ-transition. This transition occurs around 2.17 K and shows an anomalous variation of the heat capacity c_V as shown in Figure 3. Because of the shape of the c_V curve in the figure, this transition is named as the λ-transition.

The liquid HeI behaves like a fairly normal liquid whereas the liquid HeII shows some anomalous behaviours. For example, the liquid HeII has practically zero entropy, zero viscosity and flows without resistance through a fine capillary. In order to explain these peculiar properties, Tisza propounded two fluid theory where HeII was considered to be mixture of two fluids − a normal fluid and a super fluid, and the anomalous behaviours were assigned to the super fluid. The relative amount of the two fluids in HeII depends on the temperature. The proportion of the super fluid was considered to increase from zero (at the transition temperature T_λ between HeI and HeII) to unity at absolute zero. However, the two fluid theory does not provide a complete understanding of HeII as it has no molecular basis.

Let us discuss the molecular theory to understand the behaviour of liquid He^4. London assumed He^4 as an ideal Bose-Einstein gas following the Bose-Einstein statistics. The Bose temperature is

$$T_B = \Big(\frac{h^2}{2\pi mk}\Big)\Big(\frac{N}{2.612V}\Big)^{2/3}$$

For the liquid He^4, we have,

Avogadro Number $N = 6.023 \times 10^{23}$ particles per mol

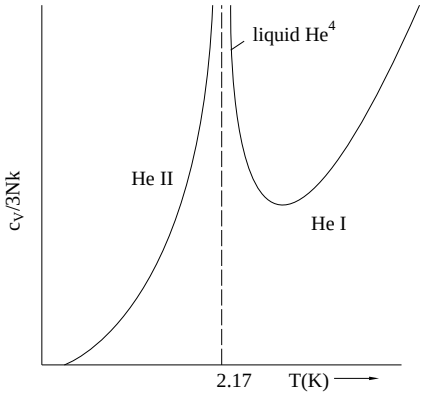


Figure 3: Variation of c_V/Nk versus T for He^4 (not to the scale).

Molar volume of helium at critical temperature $V = 27.4 \times 10^{-6}$ m^3

Mass of He^4 $m = 6.65 \times 10^{-27}$ kg

$$T_B = \Big(\frac{(6.63 \times 10^{-34})^2}{2 \times 3.14 \times (6.65 \times 10^{-27}) \times (1.38 \times 10^{-23})}\Big)$$

$$\times \Big(\frac{6.023 \times 10^{23}}{2.612 \times (27.4 \times 10^{-6})}\Big)^{2/3} = 3.15\text{K}$$

which is not far from the experimental value $T_\lambda = 2.17$ K. In the region $T \leq T_B$, the Bose gas shows some specific behaviour.

Following ideal Bose gas model, for $T \leq T_B$, the liquid He^4 can be considered as a mixture of a gaseous phase of N_e particles in the excited states and a condensed phase of N_0 particles in the ground state. According to Bose-Einstein condensation, for $T \leq T_B$, particles accumulate in the ground state and correspond to the super-fluid component of liquid HeII. On the other hand, the particles in the excited states correspond to the normal component of liquid HeII. For $T \leq T_B$, we have the number of particles in the normal component

$$N_I = N\Big(\frac{T}{T_B}\Big)^{3/2}$$

and the number of particles in the super-fluid component

$$N_{II} = N\Big[1 - \Big(\frac{T}{T_B}\Big)^{3/2}\Big]$$

showing that at $T = 0$, we only super-fluid component whereas at $T = T_B$, we have only normal component.

6.1 Thermodynamic properties at $T < T_B$

For Bose-Einstein statistics, at $T < T_B$, we have

$$\frac{U}{N_e} = \frac{(3/2)\ kT(gV/\lambda^3)g_{5/2}(1)}{(gV/\lambda^3)g_{3/2}(1)}$$

or

$$U = 0.770\ N_e kT = 0.770NkT\Big(\frac{T}{T_B}\Big)^{3/2}$$

(i) Specific heat at constant volume c_V is

$$c_V = \Big[\frac{\partial U}{\partial T}\Big]_V = 1.925Nk\Big(\frac{T}{T_B}\Big)^{3/2}$$

(ii) The entropy S is

$$S = \int_0^T \frac{c_V}{T}\ \mathrm{d}T = \int_0^T 1.925Nk\ \frac{T^{1/2}}{T_B^{3/2}}\ \mathrm{d}T = 1.283\ Nk\Big(\frac{T}{T_B}\Big)^{3/2}$$

(iii) Helmholtz free energy is

$$F = U - ST = 0.770\ \frac{NkT^{5/2}}{T_B^{3/2}} - 1.283\ \frac{NkT^{5/2}}{T_B^{3/2}} = -0.513\ \frac{NkT^{5/2}}{T_B^{3/2}}$$

(iv) Pressure is

$$P = \frac{2}{3}\ \frac{U}{V}$$

Thus, we have the equation of state

$$PV = 0.513\ \frac{NkT^{5/2}}{T_B^{3/2}}$$

7. Problems and questions

1. Discuss about the Bose-Einstein gas at high temperature.
2. Discuss about the Bose-Einstein gas at low temperature.
3. Derive thermodynamical quantities for a Bose-Einstein gas at a temperature below the Bose temperature.
4. Derive thermodynamical quantities for a Bose-Einstein gas at a temperature above the Bose temperature.

5. Derive thermodynamical quantities for phonons in a mono-atomic solid.

6. Why two isotopes, He^3 and He^4, of helium have significantly different physical properties. Discuss about the liquid He^4.

7. Show that chemical potential of a photon is zero. Obtain Planck's law for a black-body. Show that Wien and Rayleigh-Jeans laws are special cases of Planck's law. Derive Wien's displacement law and Stefan-Boltzmann law.

8. Derive thermodynamical properties for phonons in a mono-atomic solid.

9. Write notes on the following

   (i) Liquid He^4

   (ii) The λ-transition in He^4

X. Interacting Systems

In the preceding chapters, we assumed that the constituent particles of a gas do not interact with one another and therefore the potential energy of the gas was assumed to be zero. For such a gas, called an ideal gas, the equation of state is

$$PV = NkT$$

This equation remains valid when the constituent particles in the gas are far apart from one another (*i.e.,* the gas is rarefied), so that the interaction among the particles is negligible. For the real gases, the experiments showed deviations from the equation of ideal gas.

Many scientists attempted to explain these deviations by accounting for the interactions among the constituent particles of the gas. They tried also to fit the experimental results in the form of empirical relations for the equation of state. Out of them, one important relation found is the virial equation of state which can be expressed as

$$PV = NkT\Big[1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \dots\Big]$$

where the coefficients $B(T)$, $C(T)$, $D(T)$, ... are known as the second, third, fourth, ... virial coefficients.

The first qualitative interpretation of the deviations from the ideal state of the gas was given by van der Waals in terms of intermolecular interaction, which led to the famous equation of state, known as van der Waals equation of state. The quantitative interpretation can however be given in terms of the virial coefficients. At low densities, the deviations from the ideal gas can adequately be explained with the help of the second virial coefficient. With the increase of the density, higher virial coefficients come into consideration. Here, we shall consider the classical fluids consisting of a large number of spherical particles.

1. Cluster expansion for a classical gas

Let us consider classical mono-atomic gas comprising N identical particles, each of mass m, contained in a volume V at an equilibrium tem-

perature T. The total energy E of the system is

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(q) \tag{10.1}$$

where p_i's are the momentum coordinates of the particles, and $U(q)$ the potential of the system

$$U(q) = \sum_{1 \le i < j \le N} u_{ij}(r_{ij})$$

where $u_{ij}(r_{ij})$ is the pair potential of particles i and j having relative separation $r_{ij} = \mid \vec{r_i} - \vec{r_j} \mid$, where $\vec{r_i}$ and $\vec{r_j}$ are position vectors of the particles i and j, respectively. For an ideal gas, $U(q) = 0$. Since the gas is specified by some constant values of N, V and T, it is a case of canonical ensemble. The dimensionless partition function is

$$Z = \frac{1}{N!\ h^{3N}} \int \exp(-E/kT)\ \mathrm{d}q\ \mathrm{d}p \tag{10.2}$$

which is free from the Gibbs paradox. Using equation (10.1) in (10.2), we get

$$\begin{aligned} Z &= \frac{1}{N! h^{3N}} \int \exp[-E/kT]\ \mathrm{d}p\ \mathrm{d}q \\ &= \Big[\frac{V^N}{N! h^{3N}} \int \exp\Big\{-\sum_{i=1}^{3N} \frac{p_i^2}{2mkT}\Big\}\ \mathrm{d}p\Big]\Big[\frac{1}{V^N} \int \exp\Big\{-\beta U(q)\Big\}\ \mathrm{d}q\Big] \\ &= Z_p\ Z_q \end{aligned}$$

where

$$\begin{aligned} Z_p &= \frac{V^N}{N! h^{3N}} \int \exp\Big\{-\sum_{i=1}^{3N} p_i^2/2mkT\Big\}\ \mathrm{d}p \\ &= \frac{V^N}{N! h^{3N}} \prod_{i=1}^{3N} \Big[\int \exp\Big(-\frac{p_i^2}{2mkT}\Big)\ \mathrm{d}p_i\Big] = \frac{V^N (2\pi mkT)^{3N/2}}{N! h^{3N}} \end{aligned}$$

is the partition function of the ideal gas, and

$$Z_q = \frac{1}{V^N} \int \exp\Big\{-\beta U(q)\Big\}\ \mathrm{d}q \tag{10.3}$$

is known as the configuration partition function of the gas, which is equal to unity for the ideal gas (as U becomes zero). We have

$$Z_q = \frac{1}{V^N} \int \exp\Big[-\sum_{i<j} \beta u_{ij}(r_{ij})\Big] \mathrm{d}\vec{r_1}\ \ \mathrm{d}\vec{r_2} \ldots \mathrm{d}\vec{r_N}$$

$$= \frac{1}{V^N} \int \Big\{ \prod_{i<j} \exp\Big[-\beta u_{ij}(r_{ij}) \Big] \Big\} \, \mathrm{d}\vec{r_1} \;\; \mathrm{d}\vec{r_2} \ldots \mathrm{d}\vec{r_N} \qquad (10.4)$$

where each coordinate can vary within the entire volume V of the gas. Evaluation of the integrals in Z_q is not possible. However, for the study of a real gas, the integrals need to be evaluated. Thus, we use a technique, called the cluster expansion method, discussed as the following. Let us define a function

$$\eta_{ij}(r_{ij}) \equiv \exp[-\beta u_{ij}(r_{ij})] - 1 \qquad (10.5)$$

For the ideal gas, $u_{ij}(r_{ij}) = 0$, and therefore, $\eta_{ij}(r_{ij}) = 0$. Now, using equation (10.5) in (10.4), we have

$$Z_q = \frac{1}{V^N} \int \Big\{ \prod_{i<j} (1 + \eta_{ij}) \Big\} \, \mathrm{d}\vec{r_1} \;\; \mathrm{d}\vec{r_2} \ldots \mathrm{d}\vec{r_N}$$

$$= \frac{1}{V^N} \int \Big[1 + \sum_{i<j} \eta_{ij} + \sum_{\substack{i<j \\ k<l \\ i,j \neq k,l}} \eta_{ij}\eta_{kl} + \ldots \Big] \, \mathrm{d}\vec{r_1} \;\; \mathrm{d}\vec{r_2} \ldots \mathrm{d}\vec{r_N} \qquad (10.6)$$

Usual forms of $u_{ij}(r_{ij})$ and $\eta_{ij}(r_{ij})$ as functions of r_{ij} are shown in Figures 1 and 2, respectively. It shows that $\eta_{ij}(r_{ij})$ is almost zero except when $r_{ij} \approx d$, where d is the diameter of the gas particle.

For getting the equation of state for a gas van der Waals made an assumption that the particles are rigid spheres, each of diameter d, and they attract each other with a weak force which decreases rapidly, in the following manner, as the separation r between them increases:

$$u(r) = \begin{cases} \infty & \text{when} \quad r < d \\ \\ \phi(r) & \text{when} \quad r > d \end{cases}$$

where $\phi(r)$ has a negative value. A typical variation of $u(r)$ versus r is shown in Figure 1. For this potential, the function $\eta(r)$ is[1]

$$\eta_{12} = \begin{cases} -1 & \text{when} \quad r < d \\ \\ -\phi(r)/kT & \text{when} \quad r > d \end{cases}$$

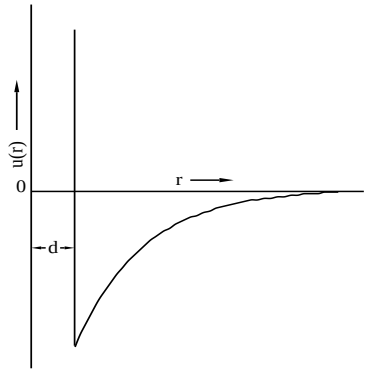


Figure 1: Variation of $u(r)$ versus r.

A typical variation of $\eta(r)$ versus r is shown in Figure 2.

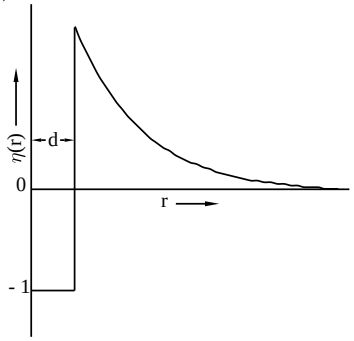


Figure 2: Variation of $\eta(r)$ versus r.

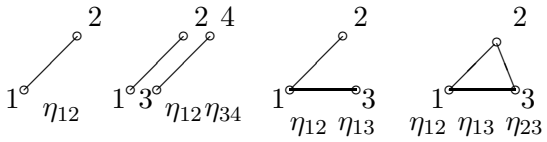


Figure 3: Some cluster terms.

Thus, the term $\eta_{ij}(r_{ij})$ contributes only when the two particles i and j are close together (binary collision), similarly, the term $\eta_{ij}(r_{ij})\eta_{jk}(r_{jk})$ contributes only when the three particles i, j and k are close together

[1]Since temperature is large, in the range of low value for $u(r)$, the exponential term in the expression for $\eta(= \mathrm{e}^{-\beta u} - 1)$ can be extended as

$$\eta = 1 - \beta u - 1 = -\beta u$$

simultaneously (triple collision), and so on. Graphical representation of such terms is shown in Figure 3. Various terms in equation (10.6) represent clusters of the particles in the gas. This representation of Z_q in the form of the series is known as the cluster expansion. Since the third, fourth, ..., terms have products of $\eta_{ij}(r_{ij})$, contributions of these terms are successively very small in comparison to the first two terms. Further, in this expansion, except for the first two integrals, the remaining integrals cannot be estimated even approximately. The first term

$$C_1 = \frac{1}{V^N} \int \mathrm{d}\vec{r}_1 \ \mathrm{d}\vec{r}_2 \ldots \mathrm{d}\vec{r}_N = 1$$

corresponds to the situation where all the interactions between the particles are neglected. That is, it corresponds to the ideal gas. Thus, when there are no interactions between the particles of the gas, we have $Z_q = 1$, and the partition function of the gas is $Z = Z_p$. The second term is

$$C_2 = \frac{1}{V^N} \int \sum_{i<j} \eta_{ij} \ \mathrm{d}\vec{r}_1 \ \mathrm{d}\vec{r}_2 \ldots \mathrm{d}\vec{r}_N$$

For N particles in the system, the sum contains in all $\frac{1}{2}N(N-1)$ terms. Since the particles are identical, interaction between two particles is of the same nature. If we choose two representative particles, denoted by 1 and 2, the sum can be approximated to $\frac{1}{2}N(N-1)\eta_{21}$ and therefore, we have

$$C_2 = \frac{N(N-1)}{2V^N} \int \eta_{12} \ \mathrm{d}\vec{r}_1 \ \mathrm{d}\vec{r}_2 \ldots \mathrm{d}\vec{r}_N$$

Now, except over $\vec{r}_1$ and $\vec{r}_2$, each integral is equal to V. Thus,

$$C_2 = \frac{N(N-1)V^{N-2}}{2V^N} \int \eta_{12} \ \mathrm{d}\vec{r}_1 \ \mathrm{d}\vec{r}_2$$

$$= \frac{N(N-1)}{2V^2} \int [\exp\{-\beta u_{12}(r_{12})\} - 1] \mathrm{d}\vec{r}_1 \ \mathrm{d}\vec{r}_2$$

For $\vec{r} = \vec{r}_2 - \vec{r}_1$, using the Jacobi transformation[2] $\mathrm{d}\vec{r}_1 \ \mathrm{d}\vec{r} = \mathrm{d}\vec{r}_1 \ \mathrm{d}\vec{r}_2$, we have

$$C_2 = \frac{N(N-1)}{2V^2} \int [\exp\{-\beta u_{12}(r_{12})\} - 1] \ \mathrm{d}\vec{r} \ \mathrm{d}\vec{r}_1$$

[2]We have $\vec{r} = \vec{r}_2 - \vec{r}_1$. Keeping the $\vec{r}_1$ unchanged and changing $\vec{r}_2$, we have $\mathrm{d}\vec{r} = \mathrm{d}\vec{r}_2$. In order to include the fact that $\vec{r}_1$ is unchanged, we write $\mathrm{d}\vec{r}_1 \ \mathrm{d}\vec{r} = \mathrm{d}\vec{r}_1 \ \mathrm{d}\vec{r}_2$.

The integration over $\vec{r}_1$ gives volume and we have

$$C_2 = \frac{N(N-1)}{2V} \int \Big[\exp\{-\beta u_{12}(r)\} - 1\Big]\, \mathrm{d}\vec{r} = \frac{N^2}{2\,V} I_2$$

where we have neglected 1 from $(N-1)$ as the number of particles N in the gas is very large, and

$$I_2 = \int \Big[\exp\{-\beta u_{12}(r)\} - 1\Big]\, \mathrm{d}\vec{r}$$

Thus, we have

$$Z_q = \Big[1 + \frac{N^2 I_2}{2\,V} + \ldots\Big] = \Big[1 + N\Big(\frac{NI_2}{2V}\Big) + \ldots\Big]$$

$$\approx \Big(1 + \frac{NI_2}{2V}\Big)^N \qquad \text{for} \qquad NI_2/2V << 1$$

The condition $NI_2/2V << 1$ is satisfied as I_2 is of the order of the volume v_0 of one particle. Thus, the partition function is

$$Z = Z_p\, Z_q = Z_p\Big(1 + \frac{NI_2}{2V}\Big)^N \tag{10.7}$$

Now, we can calculate various thermodynamical quantities.

(i) Helmholtz free energy F, using equation (10.7), is

$$F = -kT\, \ln Z = -kT\, \ln Z_p - kTN\, \ln\Big(1 + \frac{NI_2}{2V}\Big)$$

$$= F_p - kTN\, \ln\Big(1 + \frac{NI_2}{2V}\Big) \approx F_p - kTN\, \frac{NI_2}{2V} = F_p - \frac{kTN^2 I_2}{2V}$$

where F_p is the Helmholtz free energy for the ideal gas.

(ii) Pressure P of the real gas is given by

$$P = -\frac{\partial F}{\partial V} = -\frac{\partial F_p}{\partial V} - \frac{kTN^2 I_2}{2V^2}$$

$$= \frac{NkT}{V} - \frac{kTN^2 I_2}{2V^2} = \frac{NkT}{V}\Big(1 - \frac{NI_2}{2V}\Big) \tag{10.8}$$

It shows that the pressure of a real gas is smaller than that of the corresponding ideal gas. We can write the equation of state in the Virial form as

$$PV = NkT\Big(1 - \frac{NI_2}{2V}\Big)$$

It gives the Virial coefficient $B(T) = -NI_2/2$.

(iii) Entropy S of the real gas is given by

$$S = -\frac{\partial F}{\partial T} = -\frac{\partial F_p}{\partial T} + \frac{kN^2 I_2}{2V} = S_p + \frac{kN^2 I_2}{2V}$$

where S_p is the entropy for the ideal gas. It shows that the entropy of a real gas is more than that of the corresponding ideal gas.

1.1 Van der Waals equation

Let us consider that the molecules are hard spheres of diameter d. Then the limits of the integral I_2 can be divided into two parts. In the first part $0 < r < d$, the potential $u(r)$ is infinite and we have

$$\begin{aligned} I_2 &= \int_0^\infty \Big[\exp\{-\beta u\} - 1\Big]\, \mathrm{d}\vec{r} \\ &= \int_0^d \Big[\exp\{-\beta u\} - 1\Big]\mathrm{d}^3 r + \int_d^\infty \Big[\exp\{-\beta u\} - 1\Big]\mathrm{d}\vec{r} \\ &= \int_0^d (-1) 4\pi r^2 \mathrm{d}r + \int_d^\infty [(1 - \beta u + \ldots) - 1] 4\pi r^2 \, \mathrm{d}r \\ &= -4\pi \frac{d^3}{3} - \frac{4\pi}{kT}\int_d^\infty r^2 u \, \mathrm{d}r = -\frac{2b}{N} + \frac{2a}{kTN^2} \end{aligned} \tag{10.9}$$

where

$$b = \frac{2\pi d^3 N}{3} \qquad \text{and} \qquad a = -2\pi N^2 \int_d^\infty r^2 u \, \mathrm{d}r$$

Using equation (10.9) in (10.8), we get

$$\begin{aligned} P &= \frac{NkT}{V}\Big[1 - \frac{N}{2V}\Big(- \frac{2b}{N} + \frac{2a}{kTN^2}\Big)\Big] = \frac{NkT}{V}\Big(1 + \frac{b}{V}\Big) - \frac{a}{V^2} \\ &\approx \frac{NkT}{V}\Big(1 - \frac{b}{V}\Big)^{-1} - \frac{a}{V^2} \end{aligned}$$

Thus, we have

$$\begin{aligned} \Big(P + \frac{a}{V^2}\Big) &= \frac{NkT}{V}\Big(1 - \frac{b}{V}\Big)^{-1} \\ \Big(P + \frac{a}{V^2}\Big)\Big(1 - \frac{b}{V}\Big) &= \frac{NkT}{V} \\ \Big(P + \frac{a}{V^2}\Big)(V - b) &= NkT \end{aligned} \tag{10.10}$$

This is van der Waals equation for a real gas, which is theoretically correct up to the second virial coefficient. van der Waals was the first who gave qualitative interpretation for deviations for a real gas from the equation of state of an ideal gas. Values of van der Waals constants a and b for some simple gases are given the following table.

Values of a in Pa m^6/mol^2 and b in 10^{-3} m^3/mol

Gas	a	b	Gas	a	b
NH_3	0.417	0.0371	HCl	0.3716	0.04081
Ar	0.1355	0.03201	Hg	0.82	0.01696
C_6H_6	1.824	0.1154	CH_4	0.2283	0.04278
CO_2	0.364	0.04267	CH_3OH	0.9649	0.06702
CO	0.1505	0.03985	Ne	0.02135	0.01709
Cl_2	0.6579	0.05622	N_2	0.137	0.0387
He	0.00346	0.0238	O_2	0.1382	0.03186
H_2	0.02476	0.02661	H_2O	0.5536	0.03049

Equation (10.10) can be written as

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

$$PV^3 - (Pb + RT)V^2 + aV - ab = 0$$

For the given values of P and T, it is a polynomial equation of degree three in V with constant coefficients. Hence, the equation has three roots. Since for real coefficients the complex roots always appear in pair, one of the three roots would be real. The pressure can be expressed as

$$P = \frac{RTV^2 - aV + ab}{V^3 - bV^2}$$

For some given values of temperature T, variation of P versus V is shown in Figure 4. In the figure, by drawing a horizontal line $P =$ constant, roots can be obtained. All the three roots may be real or two of them may be complex. It can be found that at low temperatures, three real roots, V_1, V_2 and V_3, exist over a certain range of the value of pressure. With the increase of temperature, these real roots approach one another, and at the temperature T_c they merge into one value. Above T_c, only one real root exists for all values of the pressure (other two roots become complex). The point in the PV-diagram where three real roots merge into one real root, is known as the critical point and the temperature T_c is known as the critical temperature. The values of pressure and volume at the critical point are known as critical pressure P_c and critical volume V_c, respectively. Expressions for the critical constants, P_c, V_c and T_c, are derived in the next section.

1.2 Explanation of the discrepancy

For $T < T_c$, these theoretical curves do not match with the experimental variation of P versus V. This discrepancy between the theoretical and

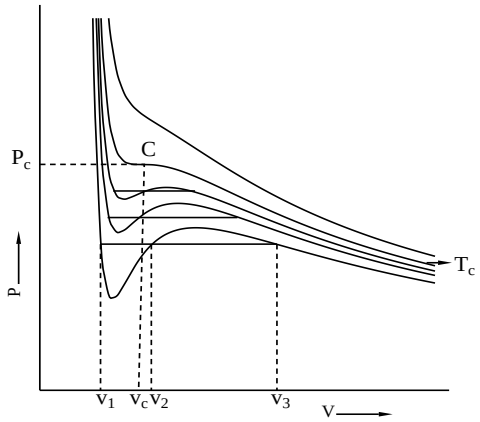


Figure 4: Variation of P versus V for some values of T for a real gas. For $T < T_c$ and a given value of pressure P, an isotherm passes through the three values V_1, V_2 and V_3 for the volume of the gas. At the critical temperature $T = T_c$, the three values merge to a single value V_c, called the critical volume. The point C, where $T = T_c$ and $V = V_c$, is known as the critical point and the corresponding pressure is known as the critical pressure P_c.

the experimental curves can be understood on the basis of the instability of equilibrium. For $T < T_c$, there is a region where $\partial P/\partial V > 0$. Physically, at constant temperature, the pressure of a gas decreases with the increase of the volume. Hence, this situation is obviously unphysical and therefore the isotherms violate the stability condition $\partial P/\partial V \leq 0$. Since we can have $\partial P/\partial V = 0$, in order to get rid of this difficulty, a horizontal variation of the curve, such that area A = area B, was proposed by Maxwell (Figure 5). This geometrical construction is known as the Maxwell construction.

Let us understand the logic behind the Maxwell proposal (construction). The Helmholtz free energy $F(T, V)$ in terms of the pressure is

$$F = -\int P \, \mathrm{d}V$$

The term on the right side of this equation is obviously the area under an isotherm in a P-V diagram. For an isotherm at $T < T_c$ in the P-V diagram [upper part of Figure 5], the free energy F versus V is plotted in the lower part of Figure 5(b). The plot has a kink in the variation of F with V. For the equilibrium situation, F should however be minimal.

In the upper part of Figure 5, the points a, c and b lie in a horizontal line (where the pressure is constant) such that the area A = area B. In the F-V diagram, the points a$'$ and b$'$ correspond to the points a and b in the P-V diagram [lower part of Figure 5]. The tangents drawn at the points a$'$ and b$'$ are found to form a common line a$'$c$'$b$'$.

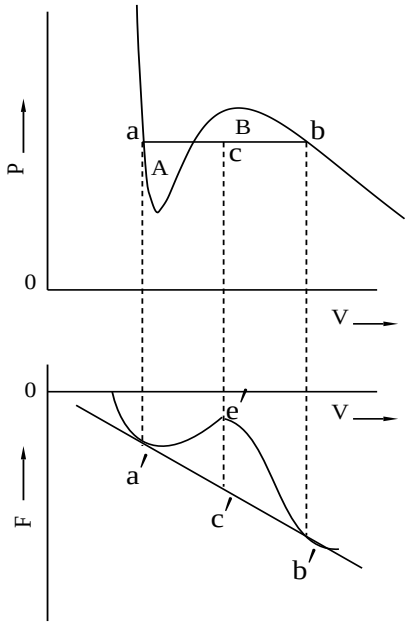


Figure 5: Maxwell construction for a van der Waals isotherm such that the area A is equal to the area B. Lower part of the figure shows that variation pf Helmholtz free energy as a function of volume V.

The concept of the Maxwell construction can be understood in the following manner. In the P-V diagram, the points a and b lie on horizontal line corresponding to a constant value of pressure. Thus, we have

$$P_a = P_b \qquad \text{thus,} \qquad -\Big(\frac{\partial F}{\partial V}\Big)_a = -\Big(\frac{\partial F}{\partial V}\Big)_b$$

Since the line a′c′b′ is a common tangent to the F-V diagram at the points a′ and b′, we can write

$$\frac{F_b - F_a}{V_b - V_a} = \Big(\frac{\partial F}{\partial V}\Big)_a$$

Thus, the relation

$$P_a = -\Big(\frac{\partial F}{\partial V}\Big)_a$$

gives

$$P_a = -\frac{F_b - F_a}{V_b - V_a} \qquad \text{or} \qquad P_a(V_b - V_a) = -(F_b - F_a) = \int_a^b P \, \mathrm{d}V$$

Since $\int_a^b P \, \mathrm{d}V$ is the area under the P-V curve and $P_a(V_b - V_a)$ is the area under the horizontal line acb, it shows that the area A is equal

to the area B. The points a and b, having the same values for P and T, can be interpreted as the pure-liquid and pure-vapour end-points, respectively. Between the points a and b, the matter is in the form of a mixture of liquid and vapour phases.

Thus, the van der Waals equation of state and Maxwell construction have been the first step to explain the behaviour of a real gas showing a deviation from the ideal gas equation.

2. Critical constants of a real gas

When temperature of a gas is below the critical temperature T_c ($T < T_c$), it can change into liquid as well as solid phases. Above the critical temperature, the gas can neither be changed into liquid phase nor the solid one. Let us consider a P-V plane containing the critical point C as shown in Figure 4 where isotherms projected on the plane are given. Slope of an isotherm is given by $(\partial P/\partial V)_T$. The critical point is the point of inflection (showing that the curve of isotherm is concave upward on the left to the critical point and is concave downward on the right). Therefore, the second derivative of P with respect to V at the critical point should be zero. (It can neither be negative showing maximum nor positive showing minimum.) Therefore, at the critical point we have

$$\Big(\frac{\partial P}{\partial V}\Big)_c = 0 \qquad \text{and} \qquad \Big(\frac{\partial^2 P}{\partial V^2}\Big)_c = 0 \tag{10.11}$$

The equation of state of a real gas is

$$\Big(P + \frac{a}{V^2}\Big)(V - b) = RT \qquad \text{or} \qquad P = \frac{RT}{V - b} - \frac{a}{V^2}$$

Therefore, we have

$$\frac{\partial P}{\partial V} = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3} \tag{10.12}$$

and

$$\frac{\partial^2 P}{\partial V^2} = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4} \tag{10.13}$$

At the critical point, $T = T_c$, $P = P_c$ and $V = V_c$, and by using equation (10.11), the equations (10.12) and (10.13) reduce to

$$-\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0 \tag{10.14}$$

and

$$\frac{2RT_c}{(V_c-b)^3}-\frac{6a}{V_c^4}=0 \tag{10.15}$$

Substituting value of $2a/V_c^3$ from equation (10.14) in (10.15), we have

$$\frac{2RT_c}{(V_c-b)^3}-\frac{3}{V_c}\frac{RT_c}{(V_c-b)^2}=0$$

$$\frac{RT_c}{(V_c-b)^2}\Big(\frac{2}{V_c-b}-\frac{3}{V_c}\Big)=0$$

so that

$$\frac{2}{V_c-b}=\frac{3}{V_c} \qquad \text{or} \qquad V_c=3b$$

Substituting the value of V_c in equation (10.14), we get

$$-\frac{RT_c}{(3b-b)^2}+\frac{2a}{27b^3}=0 \qquad \text{or} \qquad T_c=\frac{8a}{27Rb}$$

Substituting the value of V_c and T_c in the van der Waals equation at the critical point, we get

$$P_c=\frac{RT_c}{V_c-b}-\frac{a}{V_c^2}=\frac{R(8a/27Rb)}{3b-b}-\frac{a}{9b^2}=\frac{a}{27b^2}$$

Hence, the temperature, pressure, and volume at the critical point are

$$P_c=\frac{a}{27b^2}, \qquad V_c=3b, \qquad T_c=\frac{8a}{27Rb}$$

We have

$$\frac{P_cV_c}{RT_c}=\frac{(a/27b^2)3b}{R(8a/27Rb)}=\frac{3}{8}$$

It shows that for all the gases, this ratio is 3/8. For an ideal gas, this ratio must be equal to unity showing that for an ideal gas, there is no critical point.

Exercise 1. Write down conditions for a critical point in the phase diagram of a matter.

Solution: In the P-V diagram of a matter, the conditions for a critical point are as the following:

$$\Big(\frac{\partial P}{\partial V}\Big)_c=0 \qquad \text{and} \qquad \Big(\frac{\partial^2 P}{\partial V^2}\Big)_c=0$$

2.1 Reduced form of van der Waals equation

Let us define pressure, volume and temperature in the reduced from (in terms of their critical values)

$$P_r = \frac{P}{P_c} \qquad V_r = \frac{V}{V_c} \qquad T_r = \frac{T}{T_c}$$

so that

$$P = P_r P_c \qquad V = V_r V_c \qquad T = T_r T_c$$

Thus, the van der Waals equation becomes

$$\Big(P_r P_c + \frac{a}{V_r^2 V_c^2}\Big)\Big(V_r V_c - b\Big) = R T_r T_c$$

Using the values of P_c, V_c and T_c, we have

$$\Big(P_r \frac{a}{27b^2} + \frac{a}{V_r^2 9b^2}\Big)\Big(V_r 3b - b\Big) = R T_r \frac{8a}{27Rb}$$

$$\frac{a}{27b^2}\Big(P_r + \frac{3}{V_r^2}\Big)\, b\Big(3V_r - 1\Big) = \frac{8a}{27b} T_r$$

$$\Big(P_r + \frac{3}{V_r^2}\Big)\Big(3V_r - 1\Big) = 8T_r$$

This is reduced from of the van der Waals equation.

Exercise 2. What are reduced parameters for a matter in the phase diagram.

Solution: When volume, pressure and temperature are expressed in terms of their critical values, they are called reduced parameters. Suppose the critical volume, pressure and temperature are denoted by V_c, P_c, T_c, respectively. Thus, the reduced volume V_r, pressure P_r and temperature T_r are as the following.

$$P_r = \frac{P}{P_c} \qquad V_r = \frac{V}{V_c} \qquad T_r = \frac{T}{T_c}$$

Exercise 3. Consider a gas obeying Dieterici equation

$$P(V - b)\, \exp\Big(\frac{a}{VRT}\Big) = RT$$

Find out critical constants for the gas and obtain the reduced form of the equation.

Solution: The gas equation can be rearranged as

$$P = \frac{RT}{(V-b)} \exp\Big(-\frac{a}{VRT}\Big)$$

On differentiation with respect to V, we get

$$\frac{\partial P}{\partial V} = \frac{RT}{(V-b)} \exp\Big(-\frac{a}{VRT}\Big)\Big(\frac{a}{RTV^2}\Big) - \frac{RT}{(V-b)^2} \exp\Big(-\frac{a}{VRT}\Big)$$

$$= \frac{RT}{(V-b)} \exp\Big(-\frac{a}{VRT}\Big)\Big(\frac{a}{RTV^2} - \frac{1}{(V-b)}\Big)$$

$$= P\Big(\frac{a}{RTV^2} - \frac{1}{(V-b)}\Big) \tag{10.16}$$

On differentiation again with respect to V, we get

$$\frac{\partial^2 P}{\partial V^2} = \frac{\partial P}{\partial V}\Big(\frac{a}{RTV^2} - \frac{1}{(V-b)}\Big) + P\Big(-\frac{2a}{RTV^3} + \frac{1}{(V-b)^2}\Big) \tag{10.17}$$

At the critical point, $T = T_c$, $P = P_c$ and $V = V_c$, we have

$$\Big(\frac{\partial P}{\partial V}\Big)_c = 0 \qquad \text{and} \qquad \Big(\frac{\partial^2 P}{\partial V^2}\Big)_c = 0 \tag{10.18}$$

Using the fact that $P_c \neq 0$, equations (10.16), (10.17) and (10.18) give

$$\frac{a}{RT_cV_c^2} - \frac{1}{(V_c-b)} = 0 \tag{10.19}$$

and

$$-\frac{2a}{RT_cV_c^3} + \frac{1}{(V_c-b)^2} = 0 \tag{10.20}$$

Substituting value of a/RTV_c^2 from equation (10.19) in (10.20), we have

$$\frac{1}{(V_c-b)}\Big[-\frac{2}{V_c} + \frac{1}{(V_c-b)}\Big] = 0$$

so that

$$-\frac{2}{V_c} + \frac{1}{(V_c-b)} = 0 \qquad \text{or} \qquad V_c = 2b$$

Substituting the value of V_c in equation (10.19), we get

$$\frac{a}{RT_c4b^2} - \frac{1}{b} = 0 \qquad T_c = \frac{a}{4bR}$$

Substituting the values of V_c and T_c in the Dieterici equation at the critical point we get

$$P_c(V_c - b)\ \exp\Big(\frac{a}{V_c R T_c}\Big) = RT_c$$

$$P_c(2b - b)\ \exp\Big(\frac{a}{2bR(a/4bR)}\Big) = R\frac{a}{4bR}$$

$$P_c b\ \exp(2) = \frac{a}{4b} \qquad \text{or} \qquad P_c = \frac{a}{4b^2 \mathrm{e}^2}$$

We have

$$\frac{P_c V_c}{RT_c} = \frac{(a/4b^2e^2)2b}{R(a/4Rb)} = \frac{2}{\mathrm{e}^{\ 2}}$$

Now, the reduced pressure, volume and temperature are defined as

$$P_r = \frac{P}{P_c} \qquad V_r = \frac{V}{V_c} \qquad T_r = \frac{T}{T_c}$$

so that

$$P = P_r P_c \qquad V = V_r V_c \qquad T = T_r T_c$$

Using these expressions in the equation, we get

$$P_r P_c(V_r V_c - b)\ \exp\Big(\frac{a}{V_r V_c R T_r T_c}\Big) = RT_r T_c$$

Using the values of P_c, V_c and T_c, we have

$$P_r\ \frac{a}{4b^2\mathrm{e}^2}(V_r 2b - b)\ \exp\Big(\frac{a}{V_r 2bRT_r(a/4bR)}\Big) = RT_r\frac{a}{4bR}$$

or

$$P_r(2V_r - 1)\ \exp\Big(\frac{2}{V_r T_r}\Big) = \mathrm{e}^2 T_r$$

This is the reduced form of equation.

Exercise 4. Consider a gas obeying the equation of state

$$\Big(P + \frac{a}{V^3}\Big)(V - b) = RT$$

Find out critical constants for the gas and obtain the reduced form of the equation.

Solution: The gas equation can be rearranged as

$$P = \frac{RT}{V - b} - \frac{a}{V^3} \tag{10.21}$$

Therefore, we have

$$\frac{\partial P}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{3a}{V^4} \tag{10.22}$$

and

$$\frac{\partial^2 P}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{12a}{V^5} \tag{10.23}$$

At the critical point, $T = T_c$, $P = P_c$ and $V = V_c$, and equations (10.22) and (10.23) reduce to

$$-\frac{RT_c}{(V_c-b)^2} + \frac{3a}{V_c^4} = 0 \tag{10.24}$$

and

$$\frac{2RT_c}{(V_c-b)^3} - \frac{12a}{V_c^5} = 0 \tag{10.25}$$

Substituting value of $3a/V_c^4$ from equation (10.24) in (10.25), we have

$$\frac{2RT_c}{(V_c-b)^3} - \frac{4}{V_c}\frac{RT_c}{(V_c-b)^2} = 0$$

$$\frac{2RT_c}{(V_c-b)^2}\Big(\frac{1}{V_c-b} - \frac{2}{V_c}\Big) = 0$$

so that

$$\frac{1}{V_c-b} = \frac{2}{V_c} \qquad \text{or} \qquad V_c = 2b$$

Substituting the value of V_c in equation (10.24), we get

$$-\frac{RT_c}{(2b-b)^2} + \frac{3a}{16b^4} = 0 \qquad \text{or} \qquad T_c = \frac{3a}{16Rb^2}$$

Substituting the value of V_c and T_c in the van der Waals equation at the critical point, we get

$$P_c = \frac{RT_c}{V_c-b} - \frac{a}{V_c^3} = \frac{R(3a/16Rb^2)}{2b-b} - \frac{a}{8b^3} = \frac{a}{16b^3}$$

Hence, the temperature, pressure, and volume at the critical point are

$$P_c = \frac{a}{16b^3}, \qquad V_c = 2b, \qquad T_c = \frac{3a}{16Rb^2}$$

We have

$$\frac{P_cV_c}{RT_c} = \frac{(a/16b^3)2b}{R(3a/16Rb^2)} = \frac{2}{3}$$

Now, the reduced pressure, volume and temperature are defined as

$$P_r = \frac{P}{P_c} \qquad V_r = \frac{V}{V_c} \qquad T_r = \frac{T}{T_c}$$

so that

$$P = P_rP_c \qquad V = V_rV_c \qquad T = T_rT_c$$

Using these expressions in the equation, we get

$$\Big(P_rP_c + \frac{a}{V_r^3V_c^3}\Big)(V_rV_c - b) = RT_rT_c$$

Using the values of P_c, V_c and T_c, we have

$$\Big(P_r\ \frac{a}{16b^3} + \frac{a}{V_r^3 8b^3}\Big)(V_r 2b - b) = RT_r\frac{3a}{16Rb^2}$$

or

$$\Big(P_r + \frac{2}{V_r^3}\Big)(2V_r - 1) = 3RT_r$$

This is the reduced form of the equation.

3. Virial equation

Equation of state of a gas, expressed in the form

$$PV = NkT\Big[1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \dots\Big]$$

is known as the Virial equation, and the parameters $B(T)$, $C(T)$, $D(T)$, ... are known as Virial coefficients. Expressions for the Virial coefficients for van der Waals equation can be obtained in the following manner. Let us start from the van der Waals equation

$$\Big(P + \frac{a}{V^2}\Big)(V - b) = RT \qquad \Big(P + \frac{a}{V^2}\Big)V\Big(1 - \frac{b}{V}\Big) = RT$$

$$PV + \frac{a}{V} = RT\Big(1 - \frac{b}{V}\Big)^{-1} \qquad PV = RT\Big(1 - \frac{b}{V}\Big)^{-1} - \frac{a}{V}$$

$$PV = RT\Big(1 + \frac{b}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots\Big) - \frac{a}{V}$$

$$PV = RT\Big[1 + \frac{1}{V}\Big(b - \frac{a}{RT}\Big) + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots\Big]$$

Thus, for a real gas, Virial coefficients are

$$B(T) = b - \frac{a}{RT}, \qquad C(T) = b^2, \qquad D(T) = b^3, \qquad \dots$$

Exercise 5. Consider a gas obeying Dieterici equation

$$P(V - b)\,\exp\Big(\frac{a}{VRT}\Big) = RT$$

Find out the Virial coefficients for the gas.

Solution: The Dieterici equation can be rearranged in the form

$$PV\Big(1 - \frac{b}{V}\Big)\,\exp\Big(\frac{a}{VRT}\Big) = RT$$

$$PV = RT\Big(1 - \frac{b}{V}\Big)^{-1}\exp\Big(-\frac{a}{VRT}\Big)$$

$$= RT\Big[1 + \frac{b}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots\Big]$$

$$\times\Big[1 - \frac{a}{VRT} + \frac{a^2}{2V^2R^2T^2} - \frac{a^3}{6V^3R^3T^3} + \dots\Big]$$

$$= RT\Big[1 + \frac{1}{V}\Big(b - \frac{a}{RT}\Big) + \frac{1}{V^2}\Big(\frac{a^2}{2R^2T^2} - \frac{ab}{RT} - b^2\Big)$$

$$+\frac{1}{V^3}\Big(-\frac{a^3}{6R^3T^3} + \frac{a^2b}{2R^2T^2} - \frac{ab^2}{RT} + b^3\Big) + \dots\Big]$$

Hence, the Virial coefficients are

$$B(T) = b - \frac{a}{RT} \qquad\qquad C(T) = \frac{a^2}{2R^2T^2} - \frac{ab}{RT} - b^2$$

$$D(T) = -\frac{a^3}{6R^3T^3} + \frac{a^2b}{2R^2T^2} - \frac{ab^2}{RT} + b^3 \qquad\qquad \dots$$

4. Problems and questions

1. Show that pressure for a real gas can be expressed as

$$P = \frac{NkT}{V} + \frac{NkT}{V^2}\ B(T)$$

where

$$B(T) = -\frac{N}{2}\int [\mathrm{e}^{-\beta u(r)} - 1]\ \mathrm{d}\vec{r}$$

2. What is Maxwell construction for a real gas? Explain it.

3. Derive the van der Waals equation for a real gas. How the discrepancy at $T < T_c$ between the theoretical curves for P versus V and the experimental results can be removed?

4. Obtain expressions for the Virial coefficients when the gas is expressed by the van der Waals equation

$$\Big(P + \frac{a}{V^2}\Big)(V - b) = RT$$

5. Obtain expressions for the Virial coefficients when the gas is expressed by the Dieterici equation

$$P(V - b)\ \exp\Big(\frac{a}{VRT}\Big) = RT$$

6. Obtain expressions for critical temperature, critical pressure and critical volume when the gas is expressed by the van der Waals equation

$$\Big(P + \frac{a}{V^2}\Big)(V - b) = RT$$

Does, for an ideal gas, there exists a critical point.

7. Obtain expressions for critical temperature, critical pressure and critical volume when the gas is expressed by the Dieterici equation

$$P(V - b)\ \exp\Big(\frac{a}{VRT}\Big) = RT$$

Does, for an ideal gas, there exists a critical point.

8. For the van der Waals equation

$$\Big(P + \frac{a}{V^2}\Big)(V - b) = RT$$

show that at the critical point we have

$$\frac{P_c V_c}{RT_c} = \frac{3}{8}$$

9. For the Dieterici equation

$$P(V - b)\, \exp\Big(\frac{a}{VRT}\Big) = RT$$

show that at the critical point we have

$$\frac{P_c V_c}{RT_c} = \frac{2}{\mathrm{e}^2}$$

10. For the equation of state

$$\Big(P + \frac{a}{V^3}\Big)(V - b) = RT$$

show that at the critical point we have

$$\frac{P_c V_c}{RT_c} = \frac{2}{3}$$

11. Show that for a real gas, the pressure P is

$$P = \frac{NkT}{V}\Big(1 - \frac{NI_2}{2V}\Big)$$

where

$$I_2 = \int \Big[\exp\{-\beta u_{12}(r)\} - 1\Big]\, \mathrm{d}\vec{r}$$

12. Show that for a real gas, the entropy S is

$$S = \frac{5}{2}\, Nk + Nk\, \ln\Big[\frac{V}{N}\Big(\frac{2\pi mkT}{h^2}\Big)^{3/2}\Big] + \frac{kN^2 I_2}{2V}$$

where

$$I_2 = \int \Big[\exp\{-\beta u_{12}(r)\} - 1\Big]\, \mathrm{d}\vec{r}$$

13. Using cluster expansion technique, derive van der Waals equation.

14. Describe the cluster expansion technique for a classical gas. Show that pressure of a real gas is smaller than that of the corresponding ideal gas and entropy of a real gas is more than that of the corresponding ideal gas. Derive the van der Waals equation for a real gas.

15. Write notes on the following

    (i) van der Waals equation of state

    (ii) Maxwell construction and its justification

    (iii) Virial equation

    (iv) Critical point

    (v) Cluster expansion technique

    (vi) Critical point

XI. Phase Transitions

A matter in general can exist in three different states (phases), known as solid, liquid and gas (vapour). These three phases have quite different properties. Usually, on increasing the temperature, a solid changes into a liquid, and a liquid into a gas. In the reverse process with the decrease of temperature, a gas changes into a liquid, and a liquid into a solid. For example, the ice melts into the water, and the water changes into the vapour. In some cases, however, a solid changes directly into a gas without going through the liquid phase. Example of such material is the ammonium chloride (NH_4Cl). A solid changes into a liquid at the melting point; a liquid into a gas at the boiling point; a solid changes directly into a gas at the sublimation point. Transition of matter from one phase to another is one of the interesting problems in the statistical mechanics. Such transitions where state of the matter changes are known as first-order phase transitions. At the point of such phase transition, both the phases remain in equilibrium. In the case of a first-order phase transition, heat is released or absorbed.

In some cases, the state of the matter does not change but the arrangement of its constituent particles changes and thus the matter goes to a phase transition of another kind. This kind of phase transition is known as the second-order phase transition. In the case of a second-order phase transition, no heat is released or absorbed. However, the internal energy and specific volume change smoothly. In this chapter, we shall discuss about the first-order and second-order phase transitions.

1. First-order phase transitions

Let us consider one-component system[1], *i.e.,* a system having only one kind of constituent particles. For first order phase transitions, P-T diagram and P-V diagram are shown in Figures 1 and 2, respectively. Depending on the system, at some values for temperature and pressure, the three phases (solid, liquid and gas) of the system may be found in

[1]The constituent particles of the system are of one kind only.

equilibrium. In the P-T diagram, the line OA represents an equilibrium between solid and liquid phases, the line OB represents an equilibrium between solid and gas phases, and the line OC represents an equilibrium between liquid and gas phases. The point O where all the three phases are in equilibrium, is known as the triple point. The line OC terminates at the point C, called the critical point. Beyond this point, the gas phase cannot be converted into the liquid phase. In Figure 2, the point C is at the apex of the P-V curve at the critical temperature T_c. For the temperature $T > T_c$, the gas phase of the matter cannot be converted into the liquid phase, but for $T < T_c$, the gas phase can in general be converted into the liquid phase.

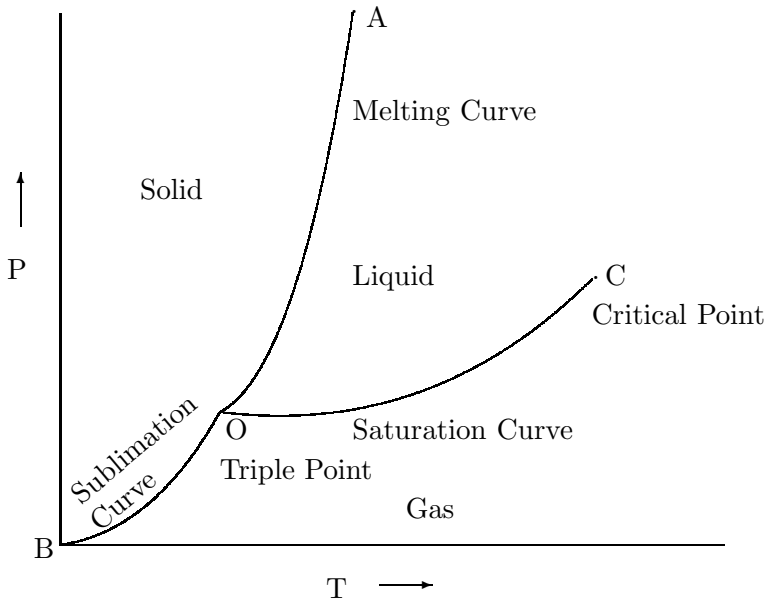


Figure 1: P-T phase diagram of one component system

Exercise 1. In the neighbourhood of the triple point of ammonia (NH_3), the sublimation curve is expressed by the relation ln P = 27.8 - 3720/T and the vapourisation curve by ln P = 24.1 - 3010/T, where the pressure P is measured in Pascal and the temperature T in Kelvin. Calculate the pressure and temperature at the triple point.

Solution: At the triple point, the pressure and temperature of the vapour,liquid and solid are the same. Let us denote them by P_t and T_t. Hence, at the triple point, we have

$$\ln P_t = 27.8 - \frac{3720}{T_t} \qquad \text{and} \qquad \ln P_t = 24.1 - \frac{3010}{T_t}$$

Therefore, from these equations, we have

$$27.8 - \frac{3720}{T_t} = 24.1 - \frac{3010}{T_t} \qquad \text{or} \qquad T_t = \frac{3720 - 3010}{27.8 - 24.1} = 191.9 \text{ K}$$

Using the value of T_t, we have

$$\ln P_t = 27.8 - \frac{3720}{191.9} = 8.41 \qquad \text{or} \qquad P_t = 4513.8 \text{ Pa}$$

Thus, the pressure and temperate at the triple point are 4.51 kPa and 191.9 K, respectively.

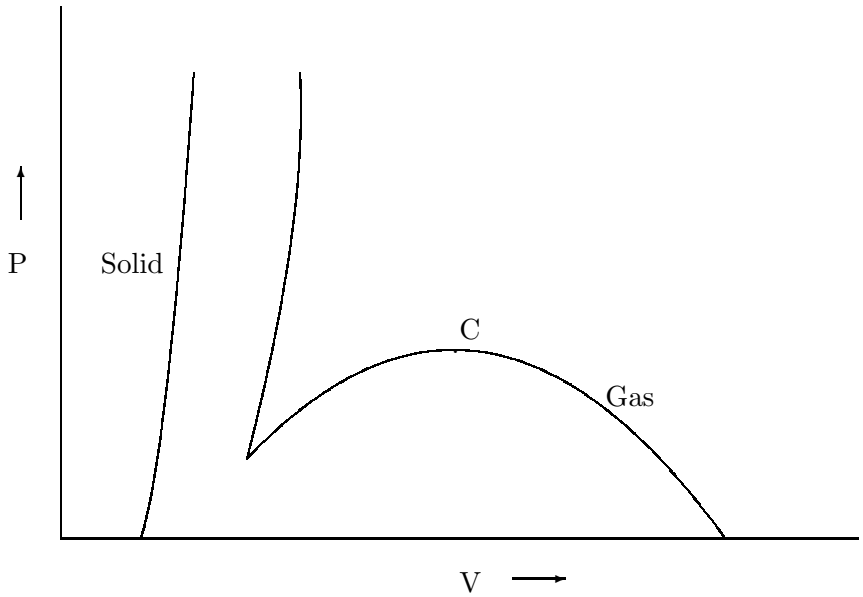


Figure 2: *P-V* phase diagram of one component system.

2. Equilibrium between two phases

Let us consider an isolated system having a matter which is existing in two phases, denoted by 1 and 2, simultaneously in equilibrium with each other (Figure 3). Suppose, V_1 and V_2 are volumes, N_1 and N_2 the number of particles, E_1 and E_2 the internal energies, and S_1 and S_2 the entropies of the two phases, respectively. For each phase, entropy is a function of its volume, number of particles (mass) and internal energy. For the phase 1 we have $S_1 = S_1(E_1, V_1, N_1)$, and therefore

$$\mathrm{d}S_1 = \frac{\partial S_1}{\partial E_1}\,\mathrm{d}E_1 + \frac{\partial S_1}{\partial V_1}\,\mathrm{d}V_1 + \frac{\partial S_1}{\partial N_1}\,\mathrm{d}N_1$$

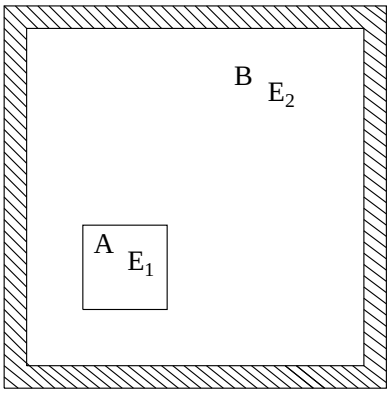


Figure 3: Equilibrium of two phases of an isolated one component system.

$$= \frac{1}{T_1}\,\mathrm{d}E_1 + \frac{P_1}{T_1}\,\mathrm{d}V_1 - \frac{\mu_1}{T_1}\,\mathrm{d}N_1 \tag{11.1}$$

where T_1, P_1 and μ_1 are, respectively, temperature, pressure and chemical potential of the matter in phase 1, and are defined as

$$\frac{1}{T_1} = \frac{\partial S_1}{\partial E_1} \qquad \frac{P_1}{T_1} = \frac{\partial S_1}{\partial V_1} \qquad -\frac{\mu_1}{T_1} = \frac{\partial S_1}{\partial N_1}$$

Similarly for the matter in phase 2, we have

$$\mathrm{d}S_2 = \frac{1}{T_2}\,\mathrm{d}E_2 + \frac{P_2}{T_2}\,\mathrm{d}V_2 - \frac{\mu_2}{T_2}\,\mathrm{d}N_2 \tag{11.2}$$

As the system having two phases of matter is isolated, total volume V, total number of particles N and total energy E of the system are constant:

$$V = V_1 + V_2 = \text{constant}$$
$$N = N_1 + N_2 = \text{constant}$$
$$E = E_1 + E_2 = \text{constant}$$

It follows that

$$\mathrm{d}V = 0 \qquad \mathrm{d}N = 0 \qquad \mathrm{d}E = 0$$

and therefore, we have

$$\mathrm{d}V_1 = -\mathrm{d}V_2 \qquad \mathrm{d}N_1 = -\mathrm{d}N_2 \qquad \mathrm{d}E_1 = -\mathrm{d}E_2 \tag{11.3}$$

Total entropy S of the system

$$S = S_1 + S_2$$

is constant in the thermodynamic equilibrium and therefore,

$$\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2 = 0 \tag{11.4}$$

Using equations (11.1) and (11.2) in (11.4), we have

$$\frac{1}{T_1}\,\mathrm{d}E_1 + \frac{P_1}{T_1}\,\mathrm{d}V_1 - \frac{\mu_1}{T_1}\,\mathrm{d}N_1 + \frac{1}{T_2}\,\mathrm{d}E_2 + \frac{P_2}{T_2}\,\mathrm{d}V_2 - \frac{\mu_2}{T_2}\,\mathrm{d}N_2 = 0 \tag{11.5}$$

Using equation (11.3) in (11.5), we get

$$\Big(\frac{1}{T_1} - \frac{1}{T_2}\Big)\,\mathrm{d}E_1 + \Big(\frac{P_1}{T_1} - \frac{P_2}{T_2}\Big)\,\mathrm{d}V_1 - \Big(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\Big)\,\mathrm{d}N_1 = 0$$

This relation is possible only when the coefficient of each $\mathrm{d}E_1$, $\mathrm{d}V_1$ and $\mathrm{d}N_1$ vanishes separately:

$$\frac{1}{T_1} - \frac{1}{T_2} = 0 \qquad \frac{P_1}{T_1} - \frac{P_2}{T_2} = 0 \qquad \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} = 0$$

From these relations, it follows that

$T_1 = T_2$	thermal equilibrium
$P_1 = P_2$	mechanical equilibrium
$\mu_1 = \mu_2$	chemical equilibrium

Hence, when two different phases of the matter are in equilibrium, their temperatures, pressures and chemical potentials must be equal. If the chemical potentials are expressed as functions of pressure and temperature, we have

$$\mu_1(P,T) = \mu_2(P,T) \tag{11.6}$$

where $P(= P_1 = P_2)$ and $T(= T_1 = T_2)$ are the common pressure and temperature, respectively, of the two phases in equilibrium. Thus, from equation (11.6), we have[2]

$$G_1(P,T)\ N_1 = G_2(P,T)\ N_2$$

where $G_1(P,T)$ and $G_2(P,T)$ are the Gibbs free energies, and N_1 and N_2 the number of particles in the two phases, respectively. When the

[2]The chemical potential per particle is the Gibbs free energy.

number of particles in the two phases are equal, we have $N_1 = N_2$ and thus, $G_1 = G_2$. On the other hand, when $N_1 > N_2$, we have $G_1 < G_2$ and when $N_1 < N_2$, we have $G_1 > G_2$. The Gibbs energies G_1 and G_2 of the two phases 1 and 2, respectively, can be exhibited as shown in Figure 4.

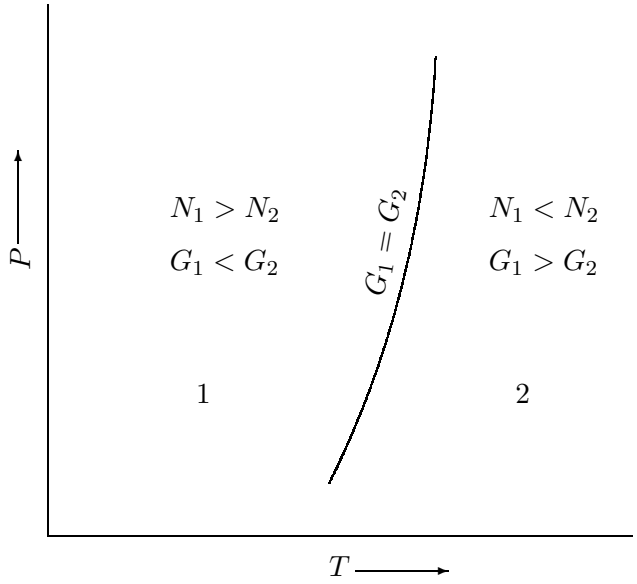


Figure 4: Phase equilibrium curve separating two phases 1 and 2.

3. Clapeyron-Clausius equation

When the two phases, denoted by 1 and 2, of the given matter are in equilibrium, we have

$$G_1(P,T) = G_2(P,T) \tag{11.7}$$

where G_1 and G_2 are Gibbs free energies of the two phases, respectively, and $P(= P_1 = P_2)$ and $T(= T_1 = T_2)$ are the common pressure and temperature, respectively, of the two phases. In the P-T diagram, along the phase-transition line, let us consider a point, where the pressure is $P + \mathrm{d}P$ and the temperature is $T + \mathrm{d}T$ so that we have

$$G_1(P + \mathrm{d}P, T + \mathrm{d}T) = G_2(P + \mathrm{d}P, T + \mathrm{d}T)$$

Using Taylor series expansion and neglecting the higher order terms, we have

$$G_1(P,T) + \frac{\partial G_1}{\partial P}\,\mathrm{d}P + \frac{\partial G_1}{\partial T}\,\mathrm{d}T = G_2(P,T) + \frac{\partial G_2}{\partial P}\,\mathrm{d}P + \frac{\partial G_2}{\partial T}\,\mathrm{d}T \quad (11.8)$$

Here, higher order terms have been neglected as their contribution is not significant. Using equation (11.7) in (11.8), we get

$$\frac{\partial G_1}{\partial P}\,\mathrm{d}P - \frac{\partial G_2}{\partial P}\,\mathrm{d}P + \frac{\partial G_1}{\partial T}\,\mathrm{d}T - \frac{\partial G_2}{\partial T}\,\mathrm{d}T = 0 \quad (11.9)$$

Molar entropy S and volume V of the substance are

$$S = -\frac{\partial G}{\partial T} \qquad \text{and} \qquad V = \frac{\partial G}{\partial P} \quad (11.10)$$

Using equation (11.10) in (11.9), we get

$$V_1\,\mathrm{d}P - V_2\,\mathrm{d}P - S_1\,\mathrm{d}T + S_2\,\mathrm{d}T = 0$$

It gives

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V} \quad (11.11)$$

This equation (11.11) is known as the Clapeyron-Clausius equation. It shows that during the first-order phase transition, change in entropy ΔS as well as change in volume ΔV both are finite. In the P-T diagram, for all the phase-transition curves, we have $\mathrm{d}P/\mathrm{d}T > 0$, and therefore, Clapeyron-Clausius equation shows that during the phase transition, with the increase of the volume, the entropy increases, and with the decrease of the volume, the entropy decreases.

In the first-order phase transition, owing to the change in volume, the density of matter changes and therefore, a certain amount of heat is either released or absorbed depending on the direction of the transition, without change in the temperature. This heat is termed as the *latent heat*[3] of the transition or simply the heat of transition. If T is the temperature, the change in entropy ΔS during the phase transition is

$$\Delta S = \frac{\Delta H}{T} = \frac{L}{T} \quad (11.12)$$

where $\Delta H (= H_2 - H_1)$ is the change in heat (enthalpy) which is the molar latent heat L. Thus, from equations (11.11) and (11.12), we have

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T\Delta V} \quad (11.13)$$

[3]The latent heat is the amount of energy given to the substance or taken from the substance without the change in its temperature. It can be possible when the volume of the matter changes. For increase of volume, the energy is supplied and for decrease of volume, the energy is taken out.

Equation (11.13) shows that the transitions where volume increases, the latent heat should be positive. That is, the heat is absorbed in the transition process. Further, when the volume decreases, the heat is released in the process.

3.1 Liquid-vapour phase transition

Let us consider a phase transition from a liquid state to a vapour one. If V_l and V_g, respectively, denote the volume in the liquid and gas phases, and L_v is the heat of vapourisation (latent heat for the transition from liquid to vapour), the Clapeyron-Clausius equation is

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L_v}{T(V_g - V_l)}$$

Since in this phase transition, V_g is always greater than V_l, and the heat of vapourisation L_v is positive and we have

$$\frac{\mathrm{d}P}{\mathrm{d}T} \rangle\ 0$$

It shows that the boiling point of a liquid increases with the increase in pressure. Now, if $V_g >> V_l$, we can neglect V_l in comparison to V_g, and we have

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L_v}{TV_g}$$

Using the ideal gas equation,[4] $PV_g = RT$, we have

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L_v P}{RT^2} \qquad \text{or} \qquad \frac{\mathrm{d}P}{P} = \frac{L_v}{R}\frac{\mathrm{d}T}{T^2}$$

On integration of this equation, we have

$$\ln P = -\frac{L_v}{R}\frac{1}{T} + C \tag{11.14}$$

where C is a constant of integration. At the critical point, we have $P = P_c$, $T = T_c$ and equation (11.14) is

$$\ln P_c = -\frac{L_v}{R}\frac{1}{T_c} + C \tag{11.15}$$

[4]Though a real gas follows the van der Waals equation, but for convenience, we can use the ideal gas equation.

On subtracting equation (11.15) from (11.14) and rearranging, we have

$$P = P_c \exp\Big[\frac{L_v}{R}\Big(\frac{1}{T_c} - \frac{1}{T}\Big)\Big]$$

Here, we have assumed that the heat of vapourisation L_v (latent heat) is independent of the temperature. However, it depends on the temperature. Suppose it varies as $L_v = a - bT$, then for an ideal gas at low pressure, we have

$$\frac{\mathrm{d}P}{P} = \frac{(a - bT)}{R}\,\frac{\mathrm{d}T}{T^2} = \frac{a}{R}\,\frac{\mathrm{d}T}{T^2} - \frac{b}{R}\,\frac{\mathrm{d}T}{T}$$

On integration of this equation, we have

$$\ln P = -\frac{a}{R}\frac{1}{T} - \frac{b}{R}\,\ln T + C \tag{11.16}$$

where C is a constant of integration. At the critical point, we have $P = P_c$, $T = T_c$ and equation (11.16) is

$$\ln P_c = -\frac{a}{R}\frac{1}{T_c} - \frac{b}{R}\,\ln T_c + C \tag{11.17}$$

On subtracting equation (11.17) from (11.16) and rearranging, we have

$$\ln\Big(\frac{P}{P_c}\Big) = \frac{a}{R}\Big(\frac{1}{T_c} - \frac{1}{T}\Big) + \frac{b}{R}\,\ln\Big(\frac{T_c}{T}\Big)$$

Exercise 2. In the phase transition from a liquid state to a vapour state, the heat of vapourisation L_v varies with temperature T as $L_v = a - bT^{1/2}$. Considering the gas as an ideal one at low pressure, show that the pressure $P(T)$ at temperature T in terms of the critical pressure $P_c(T_c)$ at critical temperature T_c is

$$\ln\Big(\frac{P}{P_c}\Big) = \frac{a}{R}\Big(\frac{1}{T_c} - \frac{1}{T}\Big) + \frac{2b}{R}\Big(\frac{1}{T^{1/2}} - \frac{1}{T_c^{1/2}}\Big)$$

Solution: Clapeyron-Clausius equation for the phase transition from liquid to vapour is

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L_v}{T(V_g - V_l)}$$

where L_v is the heat of vapourisation, and V_l and V_g, respectively, denote the volume in the liquid and gas phases. For low vapour pressure, $V_g >> V_l$

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L_v}{TV_g}$$

Using $L_v = a - bT^{1/2}$, we have

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{a - bT^{1/2}}{TV_g}$$

For an ideal gas equation, $PV_g = RT$, and thus,

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{(a - bT^{1/2})\ P}{RT^2} \qquad \text{or} \qquad \frac{\mathrm{d}P}{P} = \frac{a}{R}\frac{\mathrm{d}T}{T^2} - \frac{b}{R}\frac{\mathrm{d}T}{T^{3/2}}$$

On integration of this equation, we have

$$\ln P = -\frac{a}{R}\frac{1}{T} + 2\frac{b}{R}\frac{1}{T^{1/2}} + C \tag{11.18}$$

where C is a constant of integration. At the critical point, we have $P = P_c$, $T = T_c$ and equation (11.18) is

$$\ln P_c = -\frac{a}{R}\frac{1}{T_c} + \frac{2b}{R}\frac{1}{T_c^{1/2}} + C \tag{11.19}$$

On subtracting equation (11.19) from (11.18) and rearranging, we have

$$\ln\Big(\frac{P}{P_c}\Big) = \frac{a}{R}\Big(\frac{1}{T_c} - \frac{1}{T}\Big) + \frac{2b}{R}\Big(\frac{1}{T^{1/2}} - \frac{1}{T_c^{1/2}}\Big)$$

3.2 Solid-liquid phase transition

Let us consider a phase transition from a solid state to a liquid state. If V_s and V_l, respectively, denote the volumes in the solid and liquid phases, and L_m is the heat of melting (latent heat for the transition from solid to liquid), the Clapeyron-Clausius equation is

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L_m}{T(V_l - V_s)}$$

In this transition, volumes in the two phases are nearly equal, and two cases arise:

Case (i): when $V_l > V_s$, we have $\mathrm{d}P/\mathrm{d}T > 0$. It shows that the temperature increases with the increase in pressure. Consequently, the solid will melt easily. Most of the solids fall under this category of the phase transition.

Case (ii): when $V_l < V_s$, we have $\mathrm{d}P/\mathrm{d}T < 0$. It shows that the temperature decreases with the increase in pressure. Consequently, the solid will not melt easily. Melting of ice is an example of this category of the phase transition.

4. Critical indices

At the critical point, a number of thermodynamical quantities show anomalous behaviour. That is, a thermodynamical quantity may become infinite or zero at the critical point. One of the basic problems in the theory of phase transition is to study such thermodynamical quantities in the vicinity of the critical point. In the vicinity of the critical point, such a thermodynamical quantity X is assumed to vary as a power law of temperature difference from the critical value T_c

$$X \propto |T - T_c|^l$$

The power law of pressure difference from the critical value P_c

$$X \propto |P - P_c|^m$$

The power law of volume difference from the critical value V_c

$$X \propto |V - V_c|^n$$

Hence, the finite constant l, m or n is known as a critical exponent. These power laws are also known as the scaling laws. The value of X at the critical point becomes zero when the critical exponent is positive and becomes infinite when the critical exponent is negative. Such approach may also be called the scaling hypothesis.

As an example, the isothermal compressibility K_T, defined by

$$K_T = -\frac{1}{V}\,\frac{\partial V}{\partial P}$$

becomes infinite at the critical point. In the vicinity of T_c, K_T is represented by the power laws

$$K_T = \begin{cases} A\ |T - T_c|^{-\gamma} & T > T_c \\ \\ A'\ |T - T_c|^{-\gamma'} & T < T_c \end{cases}$$

where γ and γ' are positive constants, and are not necessarily equal to each other. For an insulating fluid, $\gamma \approx 1.1$.

As another example, the specific heat at constant volume c_V, defined by

$$c_V = \frac{\partial U}{\partial T}$$

becomes infinite at the critical point. In the vicinity of T_c, c_V is represented by the power laws

$$c_V = \begin{cases} B\ |T - T_c|^{-\alpha} & T > T_c \\ \\ B'\ |T - T_c|^{-\alpha'} & T < T_c \end{cases}$$

where α and α' are positive constants, and are not necessarily equal to each other.

Besides the singular behaviour shown above, some thermodynamical quantities reduce to zero at the critical point. For example, in the vicinity of the critical point, the difference between the liquid density ρ_l and the gas density ρ_g of a matter can be expressed as

$$\rho_l - \rho_g = C(T - T_c)^{\beta}$$

For insulating fluids, $\beta = 0.345 \pm 0.015$. Moreover in the vicinity of the critical point, we have

$$P - P_c = D(V - V_c)^{\delta}$$

For insulating fluids, δ is 4.35. It shows behaviour of some thermodynamical quantities in the vicinity of the critical point. Numerical values of the critical indices for all substances investigated so far appear to be identical. Hence, the critical indices are independent of the matter investigated. It shows the universality of the critical point behaviour. The critical exponents below and above the critical point are found to be the same

$$\gamma = \gamma' \qquad \text{and} \qquad \alpha = \alpha'$$

The critical exponents α, β, γ and δ are not independent of one another. The laws of thermodynamics can help in deriving a number of rigorous inequalities between the combinations of the critical exponents. Two of them are

$$\alpha' + 2\beta + \gamma' \geq 2 \qquad \text{and} \qquad \alpha' + \beta(\delta + 1) \geq 2$$

Exercise 3. Calculate the critical exponents α, β, δ and γ for a gas whose equation of state is expressed by the van der Waals equation.

Solution: The van der Waals equation in terms of reduced variables is

$$\Big(P_r + \frac{3}{V_r^2}\Big)\Big(3V_r - 1\Big) = 8T_r$$

where

$$P_r = \frac{P}{P_c} \qquad V_r = \frac{V}{V_c} \qquad T_r = \frac{T}{T_c}$$

and P_c, V_c, T_c are pressure, volume and temperature, respectively, at the critical point. In order to examine the neighbourhood of the critical point, let us introduce expansion parameters

$$\theta = \frac{T}{T_c} - 1 \qquad \pi = \frac{P}{P_c} - 1 \qquad \omega = \frac{V}{V_c} - 1$$

At the critical point, we have $\theta = 0$, $\pi = 0$ and $\omega = 0$. In terms of these parameters, the van der Waals equation can be expressed as

$$\left[(1+\pi) + \frac{3}{(1+\omega)^2}\right]\Big[3(1+\omega) - 1\Big] = 8(1+\theta)$$

or

$$\pi = \frac{8(1+\theta)}{3(1+\omega)-1} - \frac{3}{(1+\omega)^2} - 1 = \frac{8\theta + 16\theta\omega + 8\theta\omega^2 - 3\omega^3}{2 + 7\omega + 8\omega' + 3\omega^3} \quad (11.20)$$

(i) For the degree of the critical isotherm, δ, let us take $\theta = 0$ in equation (11.20) and expand π in terms of ω to get

$$\pi = -\frac{3}{2}\,\omega^3 + \ldots$$

Hence, the degree of of the critical isotherm is $\delta = 3$, as ω has degree 3.

(ii) For the critical exponent, γ, let us calculate $\partial\pi/\partial\omega$

$$\frac{\partial\pi}{\partial\omega} = \frac{[2 + f_1(\omega)][16\theta + f_2(\omega)] - [8\theta + f_3(\omega)][7 + f_4(\omega)]}{(2 + 7\omega + 8\omega^2 + 3\omega^3)^2}$$

where $f_1(\omega)$, $f_2(\omega)$, $f_3(\omega)$ and $f_4(\omega)$ are functions of ω and each of them becomes zero at $\omega = 0$. Putting $\omega = 0$, we obtain

$$\frac{\partial\pi}{\partial\omega} = \frac{32\theta - 56\theta}{4} = -6\theta$$

Hence, the critical exponent is $\gamma = 1$, as θ has degree 1.

(iii) For the degree of coexistence curve, β, in the neighbourhood of the critical point, the van der Waals equation can be expressed from equation (11.20) as

$$\pi = 4\theta - 6\theta\omega + 9\theta\omega^2 - \frac{3}{2}\,\omega^3 + \ldots \quad (11.21)$$

The value of ω on either side of the coexistence curve can be obtained from the conditions that along the isotherm we have

$$\int_{V_{rg}}^{V_{rl}} V_r \, \mathrm{d}P_r = 0 \qquad \text{and} \qquad P_r(V_{rg}) = P_r(V_{rl})$$

where $V_{rg} = V_g/V_c$ and $V_{rl} = V_l/V_c$ are reduced molar volumes of gas and liquid, respectively, on the coexistence curve. The condition that the pressure and temperature of liquid and gas in the coexistence region be equal gives

$$-\frac{3}{2}\,\omega_l^3 - 6\theta\omega_l + 9\theta\,\omega_l^2 = -\frac{3}{2}\,\omega_g^3 - 6\theta\omega_g + 9\theta\omega_g^2 \tag{11.22}$$

If we note that ω_l is negative and express $\omega_l = -\,\widetilde{\omega}_l$ and $\omega_g = +\,\widetilde{\omega}_g$, then equation (11.22) gives

$$4\theta(\widetilde{\omega}_l + \widetilde{\omega}_g) + 6\theta(\widetilde{\omega}_l^{\,2} + \widetilde{\omega}_g^{\,2}) + \widetilde{\omega}_l^{\,3} + \widetilde{\omega}_g^{\,3} = 0 \tag{11.23}$$

The fact that the molar Gibbs free energy of the liquid and gas phases are equal shows that

$$\int_{V_g}^{V_l} V \, \mathrm{d}P = 0 \qquad \text{or} \qquad \int_{\omega_g}^{\omega_l} \mathrm{d}\omega \, (1+\omega)\Big[-6\theta + 18\theta\omega - \frac{9}{2}\,\omega^2 + \ldots\Big] = 0$$

On integration, we have

$$-6\theta(\omega_l - \omega_g) + 6\theta(\omega_l^2 - \omega_g^2) - \frac{3}{2}\,(\omega_l^3 - \omega_g^3) + \ldots = 0$$

or

$$4\theta(\widetilde{\omega}_l + \widetilde{\omega}_g) + 4\theta(\widetilde{\omega}_l^{\,2} + \widetilde{\omega}_g^{\,2}) + \widetilde{\omega}_l^{\,3} + \widetilde{\omega}_g^{\,3} = 0 \tag{11.24}$$

Here, smaller terms have been neglected. For equations (11.23) and (11.24) to be consistent, we must have $\widetilde{\omega}_g = \widetilde{\omega}_l$. If we use this in equation (11.23) or (11.24), we get $\widetilde{\omega}_g = \widetilde{\omega}_l = \widetilde{\omega}$. This gives $\widetilde{\omega}^2 \approx -4\theta$. It may be noted that θ is negative and therefore, we have

$$\widetilde{\omega}_g \approx \widetilde{\omega}_l = 2|\theta|^{1/2} \tag{11.25}$$

and the degree of the coexistence curve is $\beta = 1/2$.

(iv) For the heat capacity exponent α, the jump in the heat capacity can be obtained in the following manner. Let us approach the critical

point along the critical isocurve, $V = V_c$. Then as $T \to T_c$, $x_l \approx x_g \to 1/2$ and $c_{Vg} \to c_{Vl}$. Thus, the jump in the heat capacity is

$$c_{vc}(T^-) - c_{vc}(T^+) = \lim_{T \to T_c} \Big[-\frac{T}{2} \Big\{ \Big(\frac{\partial P_g}{\partial V_g}\Big)_T \Big(\frac{\partial V_g}{\partial T}\Big)^2_{\text{coex}} + \Big(\frac{\partial P_l}{\partial V_l}\Big)_T \Big(\frac{\partial V_l}{\partial T}\Big)^2_{\text{coex}} \Big\} \Big]$$

Along the coexistence curve $(\partial V_r/\partial T_r)_{\text{coex}} = \pm|\epsilon|^{-1/2}$. Here, the minus sign corresponds to the liquid and the plus sign to the gas. From equations (11.21) and (11.25), we get

$$\Big(\frac{\partial P_{rl}}{\partial V_{rl}}\Big)_T \equiv \Big(\frac{\partial P_{rg}}{\partial V_{rg}}\Big)_T = 6|\epsilon| - \frac{9}{2}\,\omega^2 - 18\omega|\epsilon| + \ldots = -12|\epsilon| \pm O(\ |\epsilon|^{3/2})$$

If we note that $(P_c V_c/RT_c) = 3/8$. we get

$$c_{vc}(T^-) - c_{vc}(T^+) = \frac{9}{2}R + O(\epsilon)$$

It shows that the van der Waals equation predicts a finite jump in the heat capacity at the critical point and thus it predicts $\alpha' = \alpha = 0$.

5. Second-order phase transition

In the first-order phase transition, the state of the system changes discontinuously. For example, a solid state changes into a liquid state. But, it is also possible that the state of the matter does not change (for example, it remains solid throughout), but its configuration or symmetry changes. Such phase transitions are known as the second-order phase transitions. When some crystals are subjected to change in temperature or to an external field, they show a change in configuration or in symmetry. Such phenomena are known as the cooperative phenomena.

5.1 $BaTiO_3$

At high temperature, the ferroelectric crystal $BaTiO_3$ has a cubic structure. In the unit cell, shown in Figure 5, of the substance, Ba atoms are situated at the vertices, the O atoms at the centers of the faces, and the Ti atom at the center. An atom at a vertice of a unit cell is shared by eight adjacent unit cells. and thus, each unit cell (with eight vertices) has one Ba atom. An atom at the center of a face is shared by two adjacent unit cells, and thus, each unit cell (with six faces) has

three O atoms. Further, each unit cell has obviously one Ti atom, as it being at the center of the cell is not being shared by any other cells. As the temperature decreases below the critical value, the Ti and O atoms begin to move relative to Ba atoms, parallel to an edge of the cube. Owing to such displacements, the symmetry of the lattice changes, and it becomes tetragonal instead of cubic. Hence, the configuration of the crystal changes continuously.

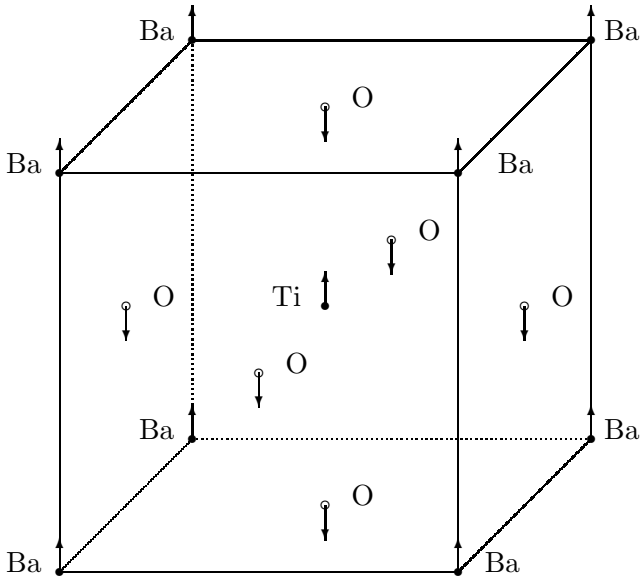


Figure 5: Cubic lattice of $BaTiO_3$.

5.2 Ferromagnetic substances

In a ferromagnetic substance, like Fe and Ni, when temperature is below the Curie temperature T_c, spins of some of its constituent atoms are spontaneously polarized in some direction, even when no external field is applied on the substance. This phenomenon is known as ferromagnetism, and a magnetization is developed. With the increase of temperature, the thermal energy of the atoms makes it possible for some of the aligned spins to flip over and to reduce the magnetization. Thus, with the increase of temperature, the ordered state of ferromagnetism destroys. As the temperature becomes larger than T_c, the spins of the constituent atoms get oriented in a random manner, and there is no more magnetization. When we go in the reverse order by decreasing the temperature, the state of random orientation of spins of the atoms at $T > T_c$ change to the state of polarization of spins in some direction at

$T < T_c$. In this transition, state of the matter remains the same (*i.e,* solid), and hence, it is known as a phase transition of second kind. Here, symmetry of the spins of the constituent atoms changes. The energies of the levels of the system are

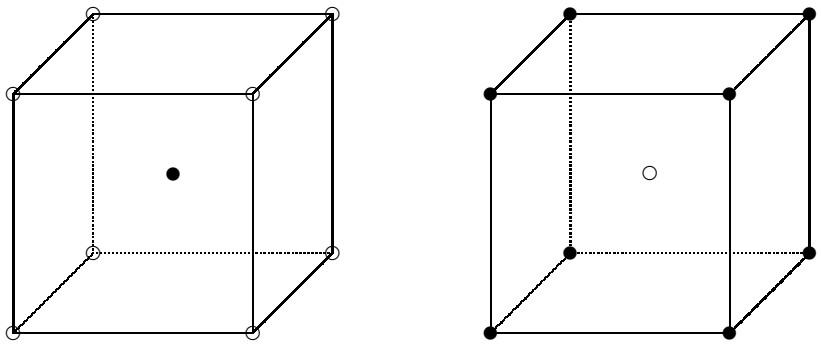
$$E = -\sum_{i,i'} \epsilon_{i,i'} \sigma_i \sigma_{i'}$$

where on each lattice site i, the spin number σ_i is $+1$ or -1, depending on the orientation of the spin and $\epsilon_{i,i'}$ is the interaction energy between the two atoms at the lattice sites i and i'.

5.3 β-brass

This is an example of the change in symmetry. For example, in an alloy AB, with the change of temperature, in the phase transition, the positions of the atoms A and B may interchange. β-brass is good example for such phase transition which is of second kind.

The β-brass is completely ordered alloy of Cu and Zn as shown in Figure 6. It has a cubic lattice where Zn atoms are at the vertices and the Cu atom at the center of the cubic cell. When this alloy is heated, it becomes disordered, and finally, the Cu and Zn atoms exchange their positions. The final lattice also is a cubic lattice where Cu atoms are at the vertices and the Zn atom at the center of the cubic cell. In this transition also the state is unchanged (*i.e.,* it is solid), hence it is a second kind transition.



(a) (b)

Figure 6: Body-centered cubic lattice of β-brass. Solid circle represents the Cu atom and the hollow circle represents the Zn atom. When the alloy (Fig. a) is heated, it becomes disordered, and finally the Cu and Zn atoms exchange their positions (Fig. b).

For the alloy AB, we may, for example, consider that $\sigma_i = +1$ for an atom A on the site i, and $\sigma_i = -1$ for an atom B on the same site i. The energies of the levels of the system are

$$E = -\sum_{i,i'} \epsilon_{i,i'}\ \sigma_i\ \sigma_{i'}$$

where on each lattice site i, the number σ_i is $+1$ or -1, depending on the occupancy of the site and $\epsilon_{i,i'}$ is the interaction energy between the two atoms at the lattice sites i and i'.

6. Ising model

Theory of second order phase transition is quite complicated, specially when a three-dimensional system is considered and all interactions are included. Ising considered that each spin interacts with the nearest neighbours only, and $\epsilon_{i,i'}$ can be taken as the average value ϵ.

6.1 One-dimensional Ising model

In one-dimensional Ising model, we account for one dimensional chain of N spins (atoms). There are two assumptions (Ising approximations): (i) each spin interacts with the nearest neighbour, and (ii) the interaction energy does not depend on the pair of atoms. Thus, in the one-dimensional case, each spin is interacting with its two nearest neighbours only. For one-dimensional configuration specified by (σ_1, σ_2, ..., σ_N), energy of the system is

$$E = -\epsilon \sum_{i=1}^{N} \sigma_i \sigma_{i+1}$$

where ϵ is the average energy of interaction between the two adjacent spins. In order to maintain continuity of the crystal, it is convenient to arrange the chain in the form of a ring so that $\sigma_{N+1} = \sigma_1$, as shown in Figure 7. The partition function is

$$Z = \sum_{\sigma_1}\sum_{\sigma_2}\ldots\sum_{\sigma_N} \exp\Big(\beta\epsilon \sum_{i=1}^{N} \sigma_i\sigma_{i+1}\Big)$$

$$= \sum_{\sigma_1}\sum_{\sigma_2}\ldots\sum_{\sigma_N} \prod_{i=1}^{N} \Big(\cosh\beta\epsilon + \sigma_i\sigma_{i+1}\sinh\beta\epsilon\Big) \qquad (11.26)$$

where each of the σ_1, σ_2, ..., σ_N can assume two values, $+1$ and -1, and $\beta = (1/kT)$. Here, we have used[5]

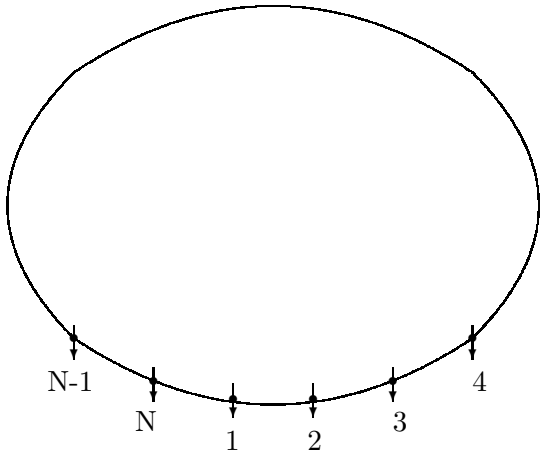


Figure 7: N Ising spins arranged in a ring so that $\sigma_{N+1} = \sigma_1$.

$$\exp(c\sigma\sigma') = \cosh c + \sigma\sigma' \sinh c$$

as $\sigma\sigma'$ can be either $+1$ or -1. Expansion of right side of equation (11.26) gives[6]

[5]When $\sigma\sigma' = 1$, we have $\exp(c\sigma\sigma') = \exp(c) = \cosh c + \sinh c = \cosh c + \sigma\sigma' \sinh c$. When $\sigma\sigma' = -1$, we have $\exp(c\sigma\sigma') = \exp(-c) = \cosh c - \sinh c = \cosh c + \sigma\sigma' \sinh c$

[6]This relation can be proved in the following manner

$$Z = \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N}\prod_{i=1}^{N}\big(\cosh\beta\epsilon + \sigma_i\sigma_{i+1}\sinh\beta\epsilon\big)$$

$$= \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N}\Big[\prod_{i=1}^{N-2}\big(\cosh\beta\epsilon + \sigma_i\sigma_{i+1}\sinh\beta\epsilon\big)\Big]\big(\cosh\beta\epsilon + \sigma_{N-1}\sigma_N\sinh\beta\epsilon\big)$$
$$\big(\cosh\beta\epsilon + \sigma_N\sigma_1\sinh\beta\epsilon\big)$$

$$= \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_{N-1}}\Big[\prod_{i=1}^{N-2}\big(\cosh\beta\epsilon + \sigma_i\sigma_{i+1}\sinh\beta\epsilon\big)\Big]\Big[\big(\cosh\beta\epsilon + \sigma_{N-1}\sinh\beta\epsilon\big)$$
$$\big(\cosh\beta\epsilon + \sigma_1\sinh\beta\epsilon\big) + \big(\cosh\beta\epsilon - \sigma_{N-1}\sinh\beta\epsilon\big)\big(\cosh\beta\epsilon - \sigma_1\sinh\beta\epsilon\big)\Big]$$

$$= 2\sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_{N-1}}\Big[\prod_{i=1}^{N-2}\big(\cosh\beta\epsilon + \sigma_i\sigma_{i+1}\sinh\beta\epsilon\big)\Big]\big(\cosh^2\beta\epsilon + \sigma_{N-1}\sigma_1\sinh^2\beta\epsilon\big)$$

$$Z = 2^N \Big[(\cosh \beta\epsilon)^N + (\sinh \beta\epsilon)^N \Big]$$

For $\beta\epsilon = \epsilon/kT \neq \infty$ $(T \neq 0)$, we have $\cosh \beta\epsilon > \sinh \beta\epsilon$. Thus, for $N >> 1$, we have

$$(\cosh \beta\epsilon)^N >> (\sinh \beta\epsilon)^N$$

and therefore,

$$Z = 2^N (\cosh \beta\epsilon)^N = (2 \cosh \beta\epsilon)^N$$

(i) The Helmholtz free energy is

$$F = -kT \ln Z = -NkT \ln\Big(2 \cosh \frac{\epsilon}{kT}\Big)$$

(ii) The entropy S is

$$S = -\frac{\partial F}{\partial T} = Nk \ln\Big(2 \cosh \frac{\epsilon}{kT}\Big) - \frac{N\epsilon}{T} \tanh\Big(\frac{\epsilon}{kT}\Big)$$

$$= 2 \sum_{\sigma_1} \sum_{\sigma_2} \cdots \sum_{\sigma_{N-1}} \Big[\prod_{i=1}^{N-3} \big(\cosh \beta\epsilon + \sigma_i \sigma_{i+1} \sinh \beta\epsilon \big) \Big] \big(\cosh \beta\epsilon + \sigma_{N-2} \sigma_{N-1} \sinh \beta\epsilon \big)$$
$$\big(\cosh^2 \beta\epsilon + \sigma_{N-1} \sigma_1 \sinh^2 \beta\epsilon \big)$$

$$= 2 \sum_{\sigma_1} \sum_{\sigma_2} \cdots \sum_{\sigma_{N-2}} \Big[\prod_{i=1}^{N-3} \big(\cosh \beta\epsilon + \sigma_i \sigma_{i+1} \sinh \beta\epsilon \big) \Big] \Big[\big(\cosh \beta\epsilon + \sigma_{N-2} \sinh \beta\epsilon \big)$$
$$\big(\cosh^2 \beta\epsilon + \sigma_1 \sinh^2 \beta\epsilon \big) + \big(\cosh \beta\epsilon - \sigma_{N-2} \sinh \beta\epsilon \big) \big(\cosh^2 \beta\epsilon - \sigma_1 \sinh^2 \beta\epsilon \big) \Big]$$

$$= 2^2 \sum_{\sigma_1} \sum_{\sigma_2} \cdots \sum_{\sigma_{N-2}} \Big[\prod_{i=1}^{N-3} \big(\cosh \beta\epsilon + \sigma_i \sigma_{i+1} \sinh \beta\epsilon \big) \Big] \big(\cosh^3 \beta\epsilon + \sigma_{N-2} \sigma_1 \sinh^3 \beta\epsilon \big)$$

This process of reduction continues and we get

$$Z = 2^{N-2} \sum_{\sigma_1} \sum_{\sigma_2} \big(\cosh \beta\epsilon + \sigma_1 \sigma_2 \sinh \beta\epsilon \big) \big(\cosh^{N-1} \beta\epsilon + \sigma_2 \sigma_1 \sinh^{N-1} \beta\epsilon \big)$$
$$= 2^{N-2} \sum_{\sigma_1} \Big[\big(\cosh \beta\epsilon + \sigma_1 \sinh \beta\epsilon \big) \big(\cosh^{N-1} \beta\epsilon + \sigma_1 \sinh^{N-1} \beta\epsilon \big)$$
$$+ \big(\cosh \beta\epsilon - \sigma_1 \sinh \beta\epsilon \big) \big(\cosh^{N-1} \beta\epsilon - \sigma_1 \sinh^{N-1} \beta\epsilon \big) \Big]$$
$$= 2^{N-1} \sum_{\sigma_1} \big(\cosh^N \beta\epsilon + \sigma_1^2 \sinh^N \beta\epsilon \big) = 2^N \big(\cosh^N \beta\epsilon + \sinh^N \beta\epsilon \big)$$

(iii) Total energy of the system is

$$U = F + ST = -N\epsilon \tanh\Big(\frac{\epsilon}{kT}\Big)$$

(iv) The specific heat at constant volume c_V is

$$c_V = \frac{\partial U}{\partial T} = \frac{N\epsilon^2}{kT^2} \operatorname{sech}^2\Big(\frac{\epsilon}{kT}\Big)$$

It shows that c_V varies with T smoothly and there is no transition temperature. Thus, one-dimensional Ising model cannot explain the ferromagnetic behaviour of a metal.

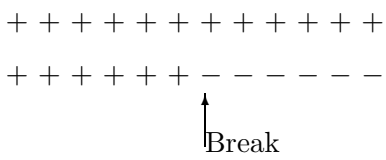


Figure 8: Long chain order in a linear chain; a single break destroys the long range order shown in the lower line.

This limitation of one-dimensional Ising model can be understood in the following manner. As shown in Figure 8, a linear chain can be easily broken at any point, and each break destroys the long-range order and increases the energy by

$$U = 2\epsilon$$

A break in the chain can be at any one of the N sites. The gain in the entropy is

$$S = k \ln N$$

and therefore, the change in free energy is

$$F = U - ST = 2\epsilon - kT \ln N$$

As the number of particles N is sufficiently large. Thus, even for low values of T, this change is always negative. Thus, the free energy is still negative and hence it has no singularity (discontinuity), which provides a phase transition phenomenon.

6.2 Two-dimensional Ising model

In a two-dimensional Ising model, we account for a square lattice (Figure 9) plain having N spins (atoms) which are perpendicular to the plane. This is a spherical surface. There are two assumptions (Ising approximations): (i) each spin interacts with the nearest neighbours, and (ii) the interaction energy does not depend on the pair of atoms. Thus, the energy of the system is

$$E = -\epsilon \sum_{k=1}^{L} \sum_{l=1}^{L} (\sigma_{kl}\sigma_{k,l+1} + \sigma_{kl}\sigma_{k+1,l}) \tag{11.27}$$

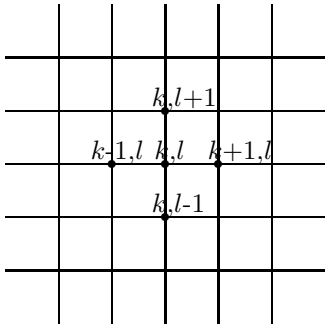


Figure 9: Two-dimensional lattice.

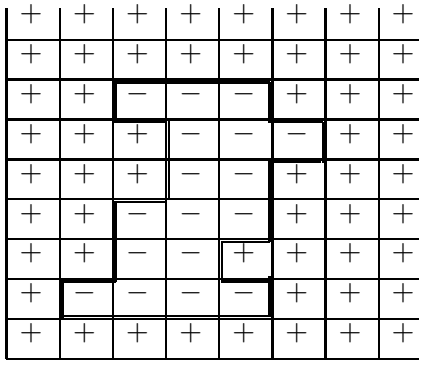


Figure 10: A connected region of reversed spins

where ϵ is the average energy of interaction between the two adjacent spins and for a square lattice $L^2 = N$. The exact evaluation of partition function for equation (11.27) is quite complicated, but is possible as shown by Onsager in 1944. Onsager found that two-dimensional Ising model can explain the ferromagnetic behaviour with the Curie temperature T_c

$$kT_c = \frac{2\epsilon}{\ln(1+\sqrt{2})} \tag{11.28}$$

An explanation to the fact that two-dimensional Ising model can explain the ferromagnetic behaviour can be given with the help of the Figure 10. In the figure we have an ordered state where the spins of one type $(-)$ are surrounded by the spins of another $(+)$ type. At the boundary of the two regions of opposite spins, suppose there are n connections of $(+\ -)$ type. Energy of the system is thus increased by

$$U = 2n\epsilon$$

At each point of the boundary, there are three degrees-of-freedom, in general. Thus, there are 3^n ways of laying down the boundary. The gain in the entropy is

$$S = k\ \ln 3^n$$

and therefore, the change in free energy is

$$F = U - ST = 2n\epsilon - kT\ \ln 3^n = n(2\epsilon - kT\ \ln 3)$$

The free energy is positive when $(kT < 2\epsilon/\ln\ 3)$ and negative when $(kT > 2\epsilon/\ln\ 3)$. Hence, the ordered state would remain stable below the Curie temperature

$$kT_c \approx \frac{2\epsilon}{\ln\ 3}$$

The correct relation is given by the equation (11.28).

6.3 Three-dimensional Ising model

Treatment of three-dimensional Ising model is too complicated and only approximate series solutions exist for it. Discussion for three-dimensional Ising model is out of the scope of this book.

7. Renormalization

Kadanoff considered that near the critical point, the spins act together in the large blocks and therefore, he introduced a concept of 'block spin transformation' for Ising ferromagnets. This concept provided a facility to work with the average spins of the large blocks instead of individual spins. Now, starting from the Ising Hamiltonian, we can describe the system in terms of an effective Hamiltonian involving only the block spins. The operation of coarse graining followed by rescaling is known as the 'renormalization group' (RG) transformation. Let us consider a system of N spins at temperature T in the absence of external magnetic field. The spins will be denoted as σ_i. Each spin can point either up ($\sigma_i = 1$) or down ($\sigma_i = -1$). The Hamiltonian H of the Ising ferromagnet is

$$H = -\epsilon \sum_{ij} \sigma_i \sigma_j \tag{11.29}$$

where $\epsilon > 0$ is the exchange interaction. The canonical partition function Z is

$$Z = \sum \mathrm{e}^{-\beta H} \tag{11.30}$$

where $\beta = 1/kT$, H the Hamiltonian and the $\sum$ in equation (11.30) stands for summation over all possible combinations $\sigma_1 = \pm 1$, $\sigma_2 = \pm 1$, etc. We define g as the negative dimensionless free energy per spin,

$$g = -\frac{F}{NkT} = \frac{1}{N} \ln Z \qquad \text{or} \qquad F = -kT \ln Z \tag{11.31}$$

where F is the Helmholtz free energy and Z the partition function of the system. For convenience, the negative sign is included such that g is usually positive.

7.1 One-dimensional Ising chain

In order to understand the process of normalization, let us consider a simple example of one dimensional Ising chain having N spins (left side of Figure 11). Defining $K = \beta\epsilon$, the canonical partition function $Z(K, N)$ of N-spin system is

$$Z(K, N) = \sum_{1}^{N} \mathrm{e}^{K(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_4 + \sigma_4\sigma_5 + \ldots)} \tag{11.32}$$

$\sigma_1 \quad \sigma_2 \quad \sigma_3 \quad \sigma_4 \quad \sigma_5 \quad \sigma_6 \quad \sigma_7 \quad \ldots \longrightarrow \quad \sigma_1 \qquad \sigma_3 \qquad \sigma_5 \qquad \sigma_7 \qquad \ldots$

Figure 11: Removal of half of the spins from one dimensional Ising chain.

Here, the summation is over N spins $\sigma_1 = \pm 1$, $\sigma_2 = \pm 1$, $\sigma_3 = \pm 1$, etc. In the Renormalization Group theory, we remove half of the spins (right side of Figure 11). This process is known as the 'decimation process'. For decimation process, we group the exponentials on the right side of equation (11.32) in pairs and thus we have

$$Z(K,N) = \sum_{1}^{N} \Big[\mathrm{e}^{K(\sigma_1\sigma_2+\sigma_2\sigma_3)}\Big]\Big[\mathrm{e}^{K(\sigma_3\sigma_4+\sigma_4\sigma_5)}\Big]\Big[\mathrm{e}^{K(\sigma_5\sigma_6+\sigma_6\sigma_7)}\Big]\ldots \quad (11.33)$$

Now, we note that σ_2 appears only in the first square bracket, σ_4 appears in the second square bracket, σ_6 appears in the third square bracket, and so on. For the first square bracket, we remove σ_2 by summing over $\sigma_2 = 1$ and $\sigma_2 = -1$; for the second square bracket, we remove σ_4 by summing over $\sigma_4 = 1$ and $\sigma_4 = -1$; and so on. Thus, we have

$$Z(K,N) = \sum_{1,3,5\ldots} \Big[\mathrm{e}^{K(\sigma_1+\sigma_3)} + \mathrm{e}^{-K(\sigma_1+\sigma_3)}\Big]\Big[\mathrm{e}^{K(\sigma_3+\sigma_5)} + \mathrm{e}^{-K(\sigma_3+\sigma_5)}\Big]$$

$$\Big[\mathrm{e}^{K(\sigma_5+\sigma_7)} + \mathrm{e}^{-K(\sigma_5+\sigma_7)}\Big]\ldots \quad (11.34)$$

Recursion relation

Now, we want to have a recursion relation from which we can compute $Z(K,N)$ for a system of N spins by using a system of $N/2$ spins (as shown as on the right side of Figure 11. With a different coupling constant K' which corresponds to a different temperature. The square bracket in equation (11.34) can be written as

$$\mathrm{e}^{K(\sigma_1+\sigma_3)} + \mathrm{e}^{-K(\sigma_1+\sigma_3)} = F(K)\ \mathrm{e}^{K'\sigma_1\sigma_3} \quad (11.35)$$

Substituting equation (11.35) in (11.32) we get

$$Z(K,N) = \sum_{1,3,5\ldots} \Big[F(K)\mathrm{e}^{K'\sigma_1\sigma_3}\Big]\Big[F(K)\mathrm{e}^{K'\sigma_3\sigma_5}\Big]\Big[F(K)\mathrm{e}^{K'\sigma_5\sigma_7}\Big]\ldots$$

$$= \Big[F(K)\Big]^{N/2} Z(K', N/2) \quad (11.36)$$

This relation gives a transformation (known as the Kadanoff transformation) from N-spin system to the $(N/2)$-spin system after removal of half of the spins. Now, we use equation (11.35) to calculate K' and $F(K$. There are obviously two possibilities for equation (11.35): (a)

$\sigma_1 = \sigma_3 = \pm 1$; (b) $\sigma_1 = -\sigma_3 = \pm 1$. For these two possibilities equation (11.35) becomes

$$e^{2K} + e^{-2K} = F(K)\ e^{K'} \qquad\qquad 2 = F(K)\ e^{-K'}$$

After solving these two equations simultaneously for K' and $F(K)$, we get

$$K' = \frac{1}{2}\ \ln\ [\cosh(2K)] \qquad \text{or} \qquad F(K) = 2\sqrt{\cosh(2K)} \quad (11.37)$$

It can be easily found that K' is always smaller than K. For $g(K)$, we have N spins whereas for $g(K')$, we have $N/2$ spins. We note that g is an intrinsic variable. Hence, equation (11.31a) should be generalized to

$$g(K) = \frac{1}{N}\ \ln\ Z(K, N) \qquad \text{and} \qquad g(K') = \frac{1}{N/2}\ \ln\ Z(K', N/2) \quad (11.38)$$

On taking logarithm on both side of equation (11.38), we get

$$\ln\ Z(K, N) = \ln\ Z(K', N/2) + \frac{N}{2}\ \ln\ F(K)$$

$$= \ln\ Z(K', N/2) + \frac{N}{2}\ \ln[2\sqrt{\cosh(2K)}]$$

Thus, we have

$$N\ g(K) = \frac{N}{2}\ g(K') + \frac{N}{2}\ \ln[2\sqrt{\cosh(2K)}]$$

and

$$2g(K) - g(K') = \ln\ F(K) = \ln[2\sqrt{\cosh(2K)}] \quad (11.39)$$

These Renormalization Group equations (11.37) and (11.39) are equivalent to as the following.

$$K' = \frac{1}{2}\ \ln\Big[\frac{e^{2K} + e^{-2K}}{2}\Big] \qquad \text{and} \qquad 2g(K) - g(K') = \ln\ 2 + K' \quad (11.40)$$

Hence, if Z and g are known for one value of K, these relations can help in finding Z and g for other values of K. We always have $K > K'$. We also note that in the high temperature limit, $K << 1$ and $K' \to K$. Then we have

$$g(K) = \ln\ 2 = 0.693 \quad (11.41)$$

Exercise 4. Apply renormalization group transformation for one dimensional Ising chain for calculating $g(1)$.

Solution: Starting from $K = 1$, we shall calculate K' and $2g(K) - g(K')$ with the help of the following equations.

$$K' = \frac{1}{2} \ln\Big[\frac{e^{2K} + e^{-2K}}{2}\Big] \qquad \text{and} \qquad 2g(K) - g(K') = \ln 2 + K' \quad (11.42)$$

This new value of K' will be used for K in the next round. The value of K will go on decreasing. This procedure will continue till K becomes very small. For this value of K, we shall take $g(K) = 0.693$ and finally calculate $g(1)$. Values of K, K', $2\ g(K) - g(K')$ obtained in various repetitions are as the following.

(a) $K = 1.000$; $K' = 0.663$; $2g(1.000) - g(0.663) = 1.356$

(b) $K = 0.663$; $K' = 0.350$; $2g(0.663) - g(0.350) = 1.043$

(c) $K = 0.350$; $K' = 0.114$; $2g(0.350) - g(0.114) = 0.807$

(d) $K = 0.114$; $K' = 0.013$; $2g(0.114) - g(0.013) = 0.706$

We can use $g(0.013) = 0.693$ (Equation 11.41) to get $g(0.114) = 0.700$, then $g(0.350) = 0.754$, $g(0.663) = 0.899$ and finally $g(1) = 1.128$. This is the same as the exact result

$$g(K) = \ln(1 + e^{-2K}) + K$$

Exercise 5. Apply renormalization group transformation for one dimensional Ising chain for calculating $g(2)$.

Solution: Starting from $K = 2$, we shall calculate K' and $2g(K) - g(K')$ with the help of the following equations.

$$K' = \frac{1}{2} \ln\Big[\frac{e^{2K} + e^{-2K}}{2}\Big] \qquad \text{and} \qquad 2g(K) - g(K') = \ln 2 + K' \quad (11.43)$$

This new value of K' will be used for K in the next round. The value of K will go on decreasing. This procedure will continue till K becomes very small. For this value of K, we shall take $g(K) = 0.693$ and finally calculate $g(2)$. Values of K, K', $2\ g(K) - g(K')$ obtained in various repetitions are as the following.

(a) $K = 2.000$; $K' = 1.654$; $2g(2.000) - g(1.654) = 2.347$

(b) $K = 1.654$; $K' = 1.308$; $2g(1.654) - g(1.308) = 2.001$

(c) $K = 1.308; \quad K' = 0.964; \quad 2g(1.308) - g(0.964) = 1.657$

(d) $K = 0.964; \quad K' = 0.628; \quad 2g(0.964) - g(0.628) = 1.321$

(e) $K = 0.628; \quad K' = 0.320; \quad 2g(0.628) - g(0.320) = 1.013$

(f) $K = 0.320; \quad K' = 0.096; \quad 2g(0.320) - g(0.096) = 0.789$

(g) $K = 0.096; \quad K' = 0.009; \quad 2g(0.096) - g(0.009) = 0.702$

We can use $g(0.009) = 0.693$ (Equation 11.43) to get $g(0.096) = 0.698$, then $g(0.320) = 0.744$, $g(0.628) = 0.879$, $g(0.964) = 1.100$, $g(1.308) = 1.379$, $g(1.654) = 1.690$, and finally $g(2) = 2.019$. This is the same as the exact result

$$g(K) = \ln(1 + \mathrm{e}^{-2K}) + K$$

7.2 Two-dimensional Ising chain

We now consider the two dimensional square Ising lattice which does not have a fixed point and phase transition (Figure 12).

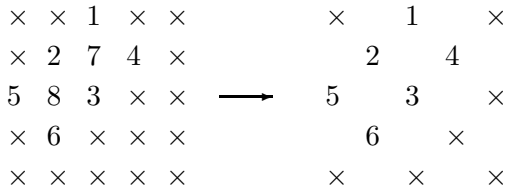


Figure 12: Removal of half of the spins from two dimensional Ising ferromagnet.

We start from the canonical partition function Z for the left side of Figure 12, where we account for the interaction between the nearest neighbours. Here, also we can remove half of the spins as shown on right side of Figure 12. The remaining spins also form a square lattice (though rotated by 45^o). For the partition function $Z(K, N)$ of the original N spin system on the left side of Figure 12, we group the exponentials in such a manner that every other spin appears only once in the exponential. For example, for removing σ_7 and σ_8 from the left side of Figure 12, we shall use

$$Z(K, N) = \sum_{1}^{N} \ldots \left[\mathrm{e}^{K\sigma_7(\sigma_1+\sigma_2+\sigma_3+\sigma_4)}\right]\left[\mathrm{e}^{K\sigma_8(\sigma_2+\sigma_7+\sigma_8+\sigma_3)}\right]\ldots$$

where the summation involves N spins. On summing over $\sigma_7 = \pm 1$ and $\sigma_8 = \pm 1$, we get

$$Z(K,N) = \sum \ldots \left[\mathrm{e}^{K(\sigma_1+\sigma_2+\sigma_3+\sigma_4)} + \mathrm{e}^{-K(\sigma_1+\sigma_2+\sigma_3+\sigma_4)} \right]$$

$$\left[\mathrm{e}^{K(\sigma_2+\sigma_5+\sigma_6+\sigma_3)} + \mathrm{e}^{-K(\sigma_2+\sigma_5+\sigma_6+\sigma_3)} \right] \ldots \qquad (11.44)$$

where the summation involves $N/2$ spins only. Similar to process followed for equation (11.35), we may write the first square bracket as

$$\mathrm{e}^{K(\sigma_1+\sigma_2+\sigma_3+\sigma_4)} + \mathrm{e}^{-K(\sigma_1+\sigma_2+\sigma_3+\sigma_4)}$$

$$= F(K)\ \mathrm{e}^{K'(\sigma_1\sigma_2+\sigma_2\sigma_3+\sigma_3\sigma_4+\sigma_4\sigma_1)} \qquad (11.45)$$

where the exponential on the right side involves nearest neighbour spins on the right side of Figure 12. However, in the two-dimensional case, this process is not acceptable as there are only two unknowns, $F(K)$ and K', for four spins. Thus, we need two more constants and we write

$$\mathrm{e}^{K(\sigma_1+\sigma_2+\sigma_3+\sigma_4)} + \mathrm{e}^{-K(\sigma_1+\sigma_2+\sigma_3+\sigma_4)}$$

$$= F(K)\ \mathrm{e}^{K_1/2(\sigma_1\sigma_2+\sigma_2\sigma_3+\sigma_3\sigma_4+\sigma_4\sigma_1)+K_2(\sigma_1\sigma_3+\sigma_2\sigma_4)+K_3(\sigma_1\sigma_2\sigma_3\sigma_4)} \qquad (11.46)$$

Here, we have $K_1/2$ for nearest neighbour interactions so that each pair of spins is repeated only once. K_2 is the coupling constant for the next nearest neighbours. There are four possibilities

(a) $\sigma_1 = \sigma_2 = \sigma_3 = \sigma_4 = \pm 1$: $\quad \mathrm{e}^{4K} + \mathrm{e}^{-4K} = F(K)\ \mathrm{e}^{2K_1+2K_2+K_3}$

(b) $\sigma_1 = \sigma_2 = \sigma_3 = -\sigma_4 = \pm 1$: $\quad \mathrm{e}^{2K} + \mathrm{e}^{-2K} = F(K)\ \mathrm{e}^{-K_3}$

(c) $\sigma_1 = \sigma_2 = -\sigma_3 = -\sigma_4 = \pm 1$: $\quad 2 = F(K)\ \mathrm{e}^{-2K_2+K_3}$

(d) $\sigma_1 = -\sigma_2 = \sigma_3 = -\sigma_4 = \pm 1$: $\quad 2 = F(K)\ \mathrm{e}^{-2K_1+2K_2+K_3}$

On solving the four equations, we get

$$F(K) = 2\ [\cosh(2K)]^{1/2}\ [\cosh(4K)]^{1/8}$$

$$K_1 = \frac{1}{4}\ \ln[\cosh(4K)] \qquad K_2 = \frac{1}{8}\ \ln[\cosh(4K)]$$

$$K_3 = \frac{1}{8}\ \ln[\cosh(4K)] - \frac{1}{2}\ \ln[\cosh(2K)] \qquad (11.47)$$

The exponential on the right side of equation (11.46) will be approximated by an Ising Hamiltonian of the square lattice. We will consider that K_1 and K_2 terms for the nearest neighbours and next nearest neighbours. For the square lattice with $N/2$ spins, there are N nearest neighbours spins. When all spins are aligned, we have $K' = K_1 + K_2$. Using equation (11.47), we get

$$K' = \frac{3}{8} \ln[\cosh(4K)] \tag{11.48}$$

It can be shown that K' is larger than K when K is larger than 0.5. Therefore, for convergence, we have not to take K larger than 0.5. Taking logarithm on both side of the relation

$$Z(K, N) = \Big[F(K)\Big]^{N/2} Z(K', N/2)$$

we get

$$\ln\, Z(K, N) = \ln\, Z(K', N/2) + \frac{N}{2} \ln\, F(K)$$

Using equation (11.38), we get

$$2g(K) - g(K') = \ln\, F(K) = \ln\Big\{2[\cosh(2K)]^{1/2}[\cosh(4K)]^{1/8}\Big\} \tag{11.49}$$

These equations (11.48) and (11.49) form a Renormalization Group for the two-dimensional square Ising ferromagnet. We also note that in the high temperature limit, $K << 1$ and $K' \to K$. Then we have

$$g(K) = \ln\, 2 = 0.693 \tag{11.50}$$

From (11.48), there is a known trivial fixed point K_c which is the solution of

$$K_c = \frac{3}{8} \ln[\cosh(4K_c)]$$

The solution is $K_c = 0.507$. Thus, $\epsilon/(kT_c) = 0.507$ where T_c is the critical temperature for the ferromagnet - paramagnet transition. This value of K_c is reasonable agreement with Onsager's exact value of $K_c = (\sinh^{-1} 1)/2 = 0.441$

Exercise 6. Apply renormalization group transformation for two dimensional Ising chain for calculating $g(0.5)$.

Solution: Starting from $K = 0.5$, we shall calculate K' and $2\ g(K) - g(K')$ with the help of the following equations.

$$K' = \frac{3}{8} \ln[\cosh(4K)]$$

and

$$2g(K) - g(K') = \ln\Big\{2[\cosh(2K)]^{1/2}[\cosh(4K)]^{1/8}\Big\}$$

This new value of K' will be used for K in the next round. The value of K will go on decreasing. This procedure will continue till K becomes very small. For this value of K, we shall take $g(K) = 0.693$ and finally calculate $g(0.5)$. Values of K, K', 2 $g(K) - g(K')$ obtained in various repetitions are as the following.

(a) $K = 0.500$; $K' = 0.497$; $2g(0.500) - g(0.497) = 1.076$

(b) $K = 0.497$; $K' = 0.492$; $2g(0.497) - g(0.492) = 1.072$

(c) $K = 0.492$; $K' = 0.486$; $2g(0.492) - g(0.486) = 1.066$

(d) $K = 0.486$; $K' = 0.476$; $2g(0.486) - g(0.476) = 1.058$

(e) $K = 0.476$; $K' = 0.463$; $2g(0.476) - g(0.463) = 1.047$

(f) $K = 0.463$; $K' = 0.444$; $2g(0.463) - g(0.444) = 1.030$

(g) $K = 0.444$; $K' = 0.416$; $2g(0.444) - g(0.416) = 1.007$

(h) $K = 0.416$; $K' = 0.377$; $2g(0.416) - g(0.377) = 0.975$

(i) $K = 0.377$; $K' = 0.324$; $2g(0.377) - g(0.324) = 0.932$

(j) $K = 0.324$; $K' = 0.253$; $2g(0.324) - g(0.253) = 0.876$

(k) $K = 0.253$; $K' = 0.166$; $2g(0.253) - g(0.166) = 0.810$

(l) $K = 0.166$; $K' = 0.078$; $2g(0.166) - g(0.078) = 0.746$

(m) $K = 0.078$; $K' = 0.018$; $2g(0.078) - g(0.018) = 0.705$

(n) $K = 0.018$; $K' = 0.001$; $2g(0.018) - g(0.001) = 0.694$

We can use $g(0.001) = 0.693$ (Equation 11.41) to get $g(0.018) = 0.694$, then $g(0.078) = 0.700$, $g(0.166) = 0.723$, $g(0.253) = 0.767$, $g(0.324) = 0.822$, $g(0.377) = 0.877$, $g(0.416) = 0.926$, $g(0.444) = 0.967$, $g(0.463) = 0.999$, $g(0.476) = 1.023$, $g(0.486) = 1.041$, $g(0.492) = 1.054$, $g(0.497) = 1.063$ and finally $g(0.5) = 1.070$.

Exercise 7. Apply renormalization group transformation for two dimensional Ising chain for calculating $g(0.4)$.

Solution: Starting from $K = 0.4$, we shall calculate K' and $2\ g(K) - g(K')$ with the help of the following equations.

$$K' = \frac{3}{8} \ln[\cosh(4K)]$$

and

$$2g(K) - g(K') = \ln\Big\{2[\cosh(2K)]^{1/2}[\cosh(4K)]^{1/8}\Big\}$$

This new value of K' will be used for K in the next round. The value of K will go on decreasing. This procedure will continue till K becomes very small. For this value of K, we shall take $g(K) = 0.693$ and finally calculate $g(0.4)$. Values of K, K', $2g(K) - g(K')$ obtained in various repetitions are as the following.

(a) $K = 0.400$; $K' = 0.355$; $2g(0.400) - g(0.355) = 0.957$

(b) $K = 0.355$; $K' = 0.294$; $2g(0.355) - g(0.294) = 0.908$

(c) $K = 0.294$; $K' = 0.215$; $2g(0.294) - g(0.215) = 0.847$

(d) $K = 0.215$; $K' = 0.124$; $2g(0.215) - g(0.124) = 0.780$

(e) $K = 0.124$; $K' = 0.045$; $2g(0.124) - g(0.045) = 0.723$

(f) $K = 0.045$; $K' = 0.006$; $2g(0.045) - g(0.006) = 0.697$

We can use $g(0.006) = 0.693$ (Equation 11.50) to get $g(0.045) = 0.695$, then $g(0.124) = 0.709$, $g(0.215) = 0.745$, $g(0.294) = 0.796$, $g(0.355) = 0.824$ and finally $g(0.4) = 0.905$.

8. Landau theory

Consider a system in a symmetric state. Suppose due to the change in the temperature, the system changes from the symmetric state to an asymmetric state. This is second order phase transition. Let the transition between the two states of the system be expressed through an order-parameter Q which changes from its zero value for the symmetric state to a non-zero value for the asymmetric state. Thus, the Helmholtz free energy F for the system is a function of temperature T as well as

Q. For a given temperature, in the thermal equilibrium, $F(T, Q)$ is the minimum. In the phase transition, Q takes arbitrarily small value near the transition point. In the vicinity of the transition point, $F(T, Q)$ may be expanded as a polynomial of Q:

$$F(T, Q) = F_0(T) + \alpha(T)\ Q + \beta(T)\ Q^2 + \gamma(T)\ Q^3 + \delta(T)\ Q^4 + \ldots$$

where the coefficients $\alpha(T)$, $\beta(T)$, $\gamma(T)$, $\delta(T)$, ... are functions of temperature T. Now, $F_0(T)$ represents free energy of the symmetric state of the system. Since we have only two states, symmetric ($Q = 0$) and asymmetric ($Q \neq 0$), in order to avoid the effect of the sign of Q, let us take $\alpha = 0$ and $\gamma = 0$, and consider the terms up to Q^4 as

$$F(T, Q) = F_0(T) + \beta Q^2 + \delta Q^4 \tag{11.51}$$

Thus, we have

$$\frac{\partial F}{\partial Q} = 2\beta Q + 4\delta Q^3$$

For optimum value of F, we have

$$\frac{\partial F}{\partial Q} = 0 \qquad \text{or} \qquad 2Q(\beta + 2\delta Q^2) = 0$$

Thus, we can have two values of Q as

$$Q = 0 \qquad \text{and} \qquad Q = \sqrt{-\frac{\beta}{2\delta}}$$

For existence of the second value of Q, the parameters β and δ must be of opposite sign. In order to decide about the maximum and minimum, we have

$$\frac{\partial^2 F}{\partial Q^2} = 2\beta + 12\delta Q^2$$

At $Q = 0$, we have

$$\frac{\partial^2 F}{\partial Q^2} = 2\beta \qquad \text{and} \qquad F = F_0(T)$$

At $Q = \sqrt{-\beta/2\delta}$, we have

$$\frac{\partial^2 F}{\partial Q^2} = -4\beta \qquad \text{and} \qquad F = F_0(T) - \frac{\beta^2}{2\delta}$$

For the existence of a system, we should have $F(T, Q)$ to be minimum and therefore, for real value of Q, the δ should be positive, as the term $(\beta^2/2\delta)$ should be positive. However, there is freedom to choose the sign of β.

(i) For $\beta < 0$, $F(T, Q)$ maximum at $Q = 0$ and minimum at $Q = \sqrt{-\beta/2\delta}$.

(ii) For $\beta > 0$, there is minimum at $Q = 0$ and maximum at $Q = \sqrt{-\beta/2\delta}$. However, for $\beta > 0$ and $\delta > 0$, the maximum will not exist.

Variations of F versus Q for $\beta > 0$, $\beta = 0$ and $\beta < 0$ with $\delta > 0$, are shown in Figure 13. Obviously, for $\beta > 0$, the $F(T, Q)$ is minimum at $Q = 0$ and for $\beta < 0$, the $F(T, Q)$ is minimum is at $Q = \sqrt{-\beta/2\delta}$. Hence, a symmetric phase exists when $\beta > 0$ and an asymmetric phase exists when $\beta < 0$. Thus, $\beta = 0$ corresponds to the transition point. For the state expressed by equation (11.51), we have $\delta > 0$ and

$$\beta < 0 \qquad \text{for asymmetric phase}$$

$$\beta > 0 \qquad \text{for symmetric phase}$$

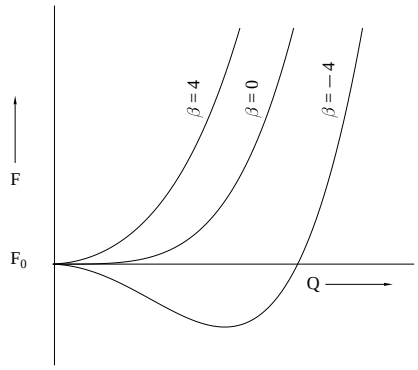


Figure 13: Variation of F versus Q for $\delta = 0.1$, and $\beta = -4$, 0 and 4. $\beta < 0$ corresponds to the symmetrical phase and $\beta > 0$ to an asymmetrical phase.

Let β and δ be expanded in the powers of $\Delta T (\equiv T - T_c)$

$$\beta(T) = \beta(T_c) + \Big(\frac{\partial \beta}{\partial T}\Big)_{T_c} (T - T_c) + \frac{1}{2}\Big(\frac{\partial^2 \beta}{\partial T^2}\Big)_{T_c} (T - T_c)^2 + \ldots$$

$$\delta(T) = \delta(T_c) + \Big(\frac{\partial \delta}{\partial T}\Big)_{T_c} (T - T_c) + \frac{1}{2}\Big(\frac{\partial^2 \delta}{\partial T^2}\Big)_{T_c} (T - T_c)^2 + \ldots$$

At the transition point $\beta(T_c) = 0$, and we approximate as

$$\beta(T) = \beta_1 (T - T_c) \qquad \text{and} \qquad \delta(T) = \delta_0$$

where

$$\beta_1 = \Big(\frac{\partial \beta}{\partial T}\Big)_{T_c} \qquad \text{and} \qquad \delta_0 = \delta(T_c)$$

It shows that $\beta(T)$ has linear dependence on T whereas $\delta(T)$ has poor dependence on T. For optimum value of F, we have

$$Q = 0 \qquad \text{and} \qquad Q = \sqrt{-\frac{\beta}{2\delta}} = \sqrt{\frac{\beta_1(T_c - T)}{2\delta_0}}$$

8.1 Thermodynamical quantities

Thermodynamical quantities of the system near the phase transition point can be calculated by using equation (11.51) as

$$F(T, Q) = F_0(T) + \beta_1(T - T_c)Q^2 + \delta_0 Q^4$$

(i) Entropy S near the phase point is

$$S = -\frac{\partial F}{\partial T} = S_0 - \beta_1 Q^2$$

where $S_0 = -(\partial F_0/\partial T)$ is the entropy for the symmetric state. The entropy for the asymmetric state is

$$S = S_0 - \beta_1\Big[\frac{\beta_1(T_c - T)}{2\delta_0}\Big] = S_0 - \frac{\beta_1^2}{2\delta_0}\,(T_c - T)$$

showing that the entropy varies smoothly at the transition point.

(ii) Total energy U is

$$U = F + TS = U_0 - \beta_1 T_c Q^2 + \delta_0 Q^4$$

where $U_0 = F_0 + TS_0$ is the total energy for the symmetric state. The total energy for the a symmetric state is

$$U = U_0 - \frac{\beta_1^2(T_c^2 - T^2)}{4\delta_0}$$

showing that total energy varies smoothly at the transition point.

(iii) The specific heat at constant volume is

$$c_V = \frac{\partial U}{\partial T} = c_{V0} + \frac{\beta_1^2 T}{2\delta_0}$$

$c_{V0} = \partial U_0/\partial T$ is the specific heat at constant volume for the symmetric state. It shows that the specific heat at constant volume varies smoothly at the transition point.

9. Problems and questions

1. Discuss about the equilibrium between two phases. Show that during a phase transition, the Gibbs energy does not change.

2. Using Clapeyron-Clausius equation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T\Delta V}$$

show that the boiling point of a liquid increases with the increase of pressure.

3. In the phase transition from a liquid state to a vapour state, the heat of vapourization L_v varies with temperature T as $L_v = a - bT^{1/2}$. Considering the gas as an ideal one, show that the pressure P at temperature T in terms of the critical pressure P_c at critical temperature T_c is

$$\ln\Big(\frac{P}{P_c}\Big) = \frac{a}{R}\Big(\frac{1}{T_C} - \frac{1}{T}\Big) + \frac{2b}{R}\Big(\frac{1}{T^{1/2}} - \frac{1}{T_c^{1/2}}\Big)$$

4. In the phase transition from a liquid state to a vapour state, the heat of vapourization L_v varies with temperature T as $L_v = a - bT^2$. Considering the gas as an ideal one, show that the pressure P at temperature T in terms of the critical pressure P_c at critical temperature T_c is

$$\ln\Big(\frac{P}{P_c}\Big) = \frac{a}{R}\Big(\frac{1}{T_C} - \frac{1}{T}\Big) + \frac{b}{R}(T - T_c)$$

5. Derive Clapeyron-Clausius equation and show that the boiling point of a liquid increases with the increase in pressure.

6. Using the Clapeyron-Clausius equation, show that when water changes into vapour, the volume increases.

7. Derive Clapeyron-Clausius equation and show that the melting point of the ice decreases with the increase in pressure.

8. Show that in the liquid-vapour phase transition, the pressure increases with the increase of temperature.

9. Comment on the statement that melting point of a solid increases with the increase in pressure.

10. For a solid-liquid phase transition, when for a given amount of material, the volume of liquid phase is smaller than that of solid phase, show that the melting temperature decreases with the increase of pressure.

11. For a solid-liquid phase transition, when for a given amount of material, the volume of liquid phase is larger than that of solid phase, show that the melting temperature increases with the increase of pressure.

12. Discuss about the scaling hypothesis used in the vicinity of the critical point where van der Waals theory fails to predict quantitative behaviour of the gas.

13. Discuss about the second-order phase transition in $BaTiO_3$ and β-brass.

14. Write down Ising approximations. Show that one-dimensional Ising model cannot explain the ferromagnetic behaviour of a metal. Discuss the reason for it.

15. Discuss that two-dimensional Ising model can explain the ferromagnetic behaviour of a metal.

16. Discuss about the Landau theory for second order phase transition. Show that in the Landau theory, at the transition point, entropy and total energy are continuous whereas the specific heat at constant pressure is discontinuous.

17. Write notes on the following

    (i) Phase transition in the $BaTiO_3$ crystal

    (ii) Phase transition in the β-brass crystal

    (iii) Critical point and triple point

    (iv) First-order phase transition

    (v) Scaling hypothesis

    (vi) Critical indices

    (vii) Second-order phase transition

    (viii) Ising approximations

    (ix) Landau theory for second order phase transition

    (x) Latent heat

XII. Kinetic Theory of Gases

In the preceding chapters, we discussed about the properties of systems in an equilibrium state. It is not always the case that a system is in the equilibrium state. The system may not be in the equilibrium state and that situation would be discussed in the present chapter as well as in the following one. Kinetic theory, which provides the basis for the microscopic theory, of a real gas involves the dynamics of interacting particles in the gas where a detailed knowledge of particle collisions is utilized. In the present chapter, we shall discuss the kinetic theory for a dilute gas where only binary collisions (collisions between two particles) are taking place. For a dilute gas, the collisions of three or more particles can be ignored easily without loosing any useful information. However, for a dense gas, collisions of three or more particles need to be considered and the situation becomes rather complicated. Treatment of dense gases is beyond the scope of this book.

1. Boltzmann transport equation

For Boltzmann distribution function $f(\vec{r}, \vec{v}, t)$ for a real gas, Boltzmann derived an integro-differential equation. He considered a dilute gas where only binary collisions are taking place. This assumption of neglecting the collisions of three or more particles can be justified when the gas is dilute enough. For the function $f(\vec{r}, \vec{v}, t)$, the number of particles at time t in the configural space between $\vec{r}$ and $\vec{r} + \mathrm{d}\vec{r}$, and the velocity space between $\vec{v}$ and $\vec{v} + \mathrm{d}\vec{v}$ is

$$f(\vec{r}, \vec{v}, t)\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{v} \tag{12.1}$$

We know that the probability of finding the number of particles in the volume element $\mathrm{d}\vec{r}\ \ \mathrm{d}\vec{p}$ of phase space about the point $(\vec{r}, \vec{p})$ is

$$N\rho(\vec{r}, \vec{p})\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{p} \tag{12.2}$$

where $\rho(\vec{r}, \vec{p})$ is the statistical distribution function and N the total number of particles in the system. Thus, we have

$$f(\vec{r}, \vec{v}, t)\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{v} = N\rho(\vec{r}, \vec{p})\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{p} \tag{12.3}$$

For the relations between the components of velocity $\vec{v}$ and momentum $\vec{p}$,

$$p_x = mv_x \qquad p_y = mv_y \qquad p_z = mv_z$$

we have

$$\mathrm{d}\vec{p} = \mathrm{d}p_x\ \mathrm{d}p_y\ \mathrm{d}p_z = m^3 \mathrm{d}v_x\ \mathrm{d}v_y\ \mathrm{d}v_z = m^3 \mathrm{d}\vec{v} \tag{12.4}$$

where m is the mass of each particle in the gas. Equation (12.4) gives a relation between the velocity space and the momentum space. Using equation (12.4) in (12.3), we have

$$f(\vec{r}, \vec{v}, t)\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{v} = N\rho(\vec{r}, \vec{p})\ \mathrm{d}\vec{r}\ m^3 \mathrm{d}\vec{v}$$

and thus, we have

$$f(\vec{r}, \vec{v}, t) = N\rho(\vec{r}, \vec{p})m^3$$

In order to obtain an explicit expression for $f(\vec{r}, \vec{v}, t)$, let us consider the equation of motion for the distribution function in six-dimensional phase space represented by the coordinates $(\vec{r}, \vec{v})$ of a particle of the system.[1] Consider a volume element $\mathrm{d}\vec{r}\ \mathrm{d}\vec{v}$ in the phase space in which the number of phase points (particles) is varying with time. The phase points move in such a way that a particle at a phase point $(\vec{r}, \vec{v})$ at time t occupies a phase point $(\vec{r} + \vec{v}\ \mathrm{d}t, \vec{v} + \vec{a}\ \mathrm{d}t)$ at time $t + \mathrm{d}t$, where $\vec{a}$ is the acceleration of the particle due to external force acting on it. In absence of collisions between the gas particles, we have

$$f(\vec{r} + \vec{v}\ \mathrm{d}t, \vec{v} + \vec{a}\ \mathrm{d}t, t + \mathrm{d}t)\ \mathrm{d}\vec{r}\ \ \mathrm{d}\vec{v} = f(\vec{r}, \vec{v}, t)\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{v} \tag{12.5}$$

In the presence of collisions between the gas particles, this equation (12.5) does not hold as some particles are deflected from their paths due to collisions among themselves. Consequently, some of the particles at the phase point $(\vec{r}, \vec{v})$ at time t do not arrive at the phase point $(\vec{r} + \vec{v}\ \mathrm{d}t, \vec{v} + \vec{a}\ \mathrm{d}t)$ at time $t + \mathrm{d}t$. Suppose the number of particles lost due to collisions in the interval $\mathrm{d}t$ be $A\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{v}\ \mathrm{d}t$. Here, A is

[1]The six-dimensional phase space is generally represented by the coordinates $(\vec{r}, \vec{p})$ of a particle of the system. It may be replaced by $(\vec{r}, \vec{v})$ as the mass m of each constituent particle is constant.

known as the loss-coefficient. On the other side, as a result of collisions, some other particles may arrive at $(\vec{r} + \vec{v}\ \mathrm{d}t, \vec{v} + \vec{a}\ \mathrm{d}t)$ at time $t + \mathrm{d}t$. Suppose the number of particles gains due to collisions in the interval $\mathrm{d}t$ be $B\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{v}\ \mathrm{d}t$. Here, B is known as the gain-coefficient. After taking into account the collisions, equation (12.5) becomes

$$f(\vec{r} + \vec{v}\ \mathrm{d}t, \vec{v} + \vec{a}\ \mathrm{d}t, t + \mathrm{d}t)\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{v} = f(\vec{r}, \vec{v}, t)\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{v} + (B - A)\ \mathrm{d}\vec{r}\ \mathrm{d}\vec{v}\ \mathrm{d}t \tag{12.6}$$

The function on the left side of equation (12.6) can be expanded in a Taylor series about $(\vec{r}, \vec{v}, t)$ as

$$f(\vec{r} + \vec{v}\ \mathrm{d}t, \vec{v} + \vec{a}\ \mathrm{d}t, t + \mathrm{d}t) = f(\vec{r}, \vec{v}, t) + (\vec{v}\ .\nabla_r f)\ \mathrm{d}t + (\vec{a}\ .\nabla_v f)\ \mathrm{d}t + \frac{\partial f}{\partial t}\ \mathrm{d}t \tag{12.7}$$

where ∇_r and ∇_v are the gradient operators with respect to $\vec{r}$ and $\vec{v}$, respectively. Using equation (12.7) in (12.6), we get

$$\frac{\partial f}{\partial t} + \vec{v}\ .\nabla_r f + \vec{a}\ .\nabla_v f = B - A \tag{12.8}$$

where $(B - A)$ gives the change of the distribution function f, resulting from the collisions. The left side of equation (12.8) gives the net rate of change in the distribution of a flow of phase points. Hence, the right side of equation (12.8) can be defined as

$$\Big(\frac{\partial f}{\partial t}\Big)_{coll} = B - A \tag{12.9}$$

The term $(\partial f/\partial t)_{coll}$ is known as the collisional integral which represents the time rate of change of f due to collisions. Thus, the Boltzmann transport equation is

$$\frac{\partial f}{\partial t} + \vec{v}\ .\nabla_r f + \vec{a}\ .\nabla_v f = \Big(\frac{\partial f}{\partial t}\Big)_{coll}$$

An explicit expression for the collisional integral can be derived in the following manner. Let us consider a dilute gas where only binary collisions among the particles are taking place. The gas is so dilute that the collisions of three or more particles can be ignored easily. Suppose, a particle i is moving with velocity $\vec{v}_i$ be at the position $\vec{r}_i$. Let us obtain the probability that this particle collides with a particle j moving with

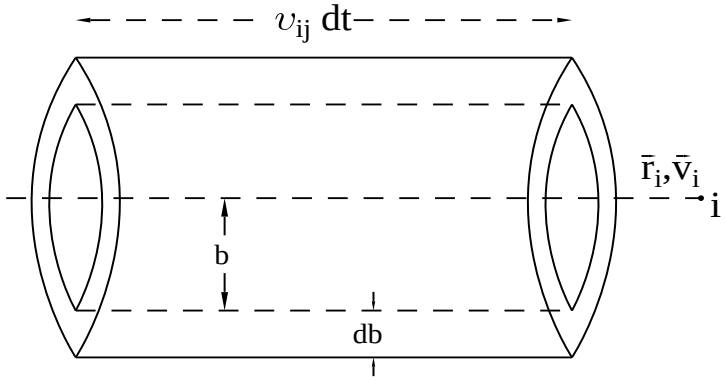


Figure 1: A particle i is taken at rest and a particle j is moving with a velocity $v_{ij}(= \mid \vec{v}_j - \vec{v}_i \mid)$ relative to that of the particle i, in the impact parameter from b to $b + \mathrm{d}b$ may collide with the particle i.

velocity $\vec{v}_j$ and lying in the impact parameter from b to $b + \mathrm{d}b$ in the time interval $\mathrm{d}t$ (Figure 1).

The velocity of the particle j relative to that of i is $(\vec{v}_j - \vec{v}_i)$. For convenience, let us assume that the particle i be at rest. Then the particle j is moving with velocity $(\vec{v}_j - \vec{v}_i)$ whose magnitude is $v_{ij} = \mid \vec{v}_j - \vec{v}_i \mid$. In the time interval $\mathrm{d}t$, the particle j travels a distance $v_{ij}\mathrm{d}t$. The volume of the cylindrical shell with inner radius b, outer radius $b + \mathrm{d}b$ and height $v_{ij}\mathrm{d}t$ is

$$\mathrm{d}V = \left[\pi(b + \mathrm{d}b)^2 - \pi b^2\right] v_{ij}\mathrm{d}t = 2\pi b \ \mathrm{d}b \ v_{ij}\mathrm{d}t$$

Here, the quadratic term in $\mathrm{d}b$ is neglected. Any particle j within the shell may collide with the particle i during the time interval $\mathrm{d}t$. The probable number of particles in this cylinder with velocities from $\vec{v}_j$ to $\vec{v}_j + \mathrm{d}\,\vec{v}_j$ is

$$f_j(\vec{r}_j, \vec{v}_j, t) 2\pi b \ \mathrm{d}b \ v_{ij}\mathrm{d}t \ \mathrm{d}\vec{v}_j$$

Thus, the total number of collisions between these particles and the particle i is

$$\mathrm{d}t \int f_j(\vec{r}_j, \vec{v}_j, t) 2\pi b v_{ij} \ \mathrm{d}b \ \mathrm{d}\vec{v}_j$$

The number of particles i in the volume element $\mathrm{d}\vec{r} \ \ \mathrm{d}\vec{v}$ about $(\vec{r}, \vec{v})$ is (distribution of particle i)

$$f_i(\vec{r}_i, \vec{v}_i, t) \ \mathrm{d}\vec{r}_i \, \mathrm{d}\vec{v}_i$$

Thus, the total number of collisions experienced by the particles i with the particles j is

$$\mathrm{d}\vec{r}_i \;\mathrm{d}\vec{v}_i \,\mathrm{d}t \int f_i(\vec{r}_i, \vec{v}_i, t) f_j(\vec{r}_j, \vec{v}_j, t) 2\pi b v_{ij} \mathrm{d}b \,\mathrm{d}\vec{v}_j \tag{12.10}$$

The coefficient A can be obtained by summing the equation (12.10) over all $\vec{v}_j$:

$$A \,\mathrm{d}\vec{r}_i \;\mathrm{d}\vec{v}_i \,\mathrm{d}t = \mathrm{d}\vec{r}_i \,\mathrm{d}\vec{v}_i \,\mathrm{d}t \sum_j \int f_i f_j 2\pi b v_{ij} \mathrm{d}b \,\mathrm{d}\vec{v}_j$$

or

$$A = \sum_j \int f_i f_j 2\pi b v_{ij} \mathrm{d}b \,\mathrm{d}\vec{v}_j \tag{12.11}$$

The coefficient B can also be obtained in a similar manner. For obtaining B, let us consider the collisions of the type $(\vec{v}_i, \vec{v}_j) \to (\vec{v}'_i, \vec{v}'_j)$. That is the particles moving with velocities $\vec{v}_i$ and $\vec{v}_j$ before collision move with the velocities $\vec{v}'_i$ and $\vec{v}'_j$, respectively after collision. Suppose for the velocities $\vec{v}'_i$ and $\vec{v}'_j$, the distribution functions are $f'_i(\vec{r}_i, \vec{v}'_i, t)$ and $f'_j(\vec{r}_j, \vec{v}'_j, t)$, respectively. The distribution functions can be used to find out the probable number of collisions which bring the particles to the region. Thus, we can write

$$B \,\mathrm{d}\vec{r}_i \,\mathrm{d}\vec{v}_i \,\mathrm{d}t = \mathrm{d}\vec{r}_i \,\mathrm{d}\vec{v}_i \,\mathrm{d}t \sum_j \int f'_i f'_j 2\pi b' v'_{ij} \;\mathrm{d}b' \;\mathrm{d}\vec{v}'_j$$

or

$$B = \sum_j \int f'_i f'_j 2\pi b' v'_{ij} \mathrm{d}b' \,\mathrm{d}\vec{v}'_j \tag{12.12}$$

For spherically symmetric potentials, we have

$$v_{ij} = v'_{ij} \qquad \text{and} \qquad b = b'$$

Further, we can take that $\mathrm{d}\vec{v}'_i \;\mathrm{d}\vec{v}'_j = \mathrm{d}\vec{v}_i \,\mathrm{d}\vec{v}_j$. With these facts, the equation (12.12) can be written as

$$B = \sum_j \int f'_i f'_j 2\pi b v_{ij} \mathrm{d}b \,\mathrm{d}\vec{v}_j$$

For a one-component gas, we have

$$A = \int f_1 f_2 2\pi b v_{12} \mathrm{d}b \,\mathrm{d}\vec{v}_2 \qquad \text{and} \qquad B = \int f'_1 f'_2 2\pi b v_{12} \mathrm{d}b \,\mathrm{d}\vec{v}_2$$

Substituting the values of A and B in equation (12.12), we have

$$\frac{\partial f_1}{\partial t} + \vec{v} \,.\nabla_r f_1 + \vec{a} \,.\nabla_v f_1 = \int (f_1' f_2' - f_1 f_2) 2\pi b v_{12} \mathrm{d}b \; \mathrm{d}\vec{v}_2 \quad (12.13)$$

This equation (12.13) is known as Boltzmann integro-differential equation for distribution function f. This equation is the basis for discussion of transport properties of gases.

2. Boltzmann H-theorem

In absence of any external force (the acceleration $\vec{a}$ is zero), the distribution function f may be considered as independent of $\vec{r}$. Thus, we have $f \equiv f(\vec{v}, t)$ and the Boltzmann integro-differential equation for one-component gas is

$$\frac{\partial f_1}{\partial t} = \int (f_1' f_2' - f_1 f_2) 2\pi b |v_2 - v_1| \mathrm{d}b \; \mathrm{d}\vec{v}_2 \quad (12.14)$$

Let us consider a function $H(t)$, known as the Boltzmann function, defined as

$$H(t) = \int f_1(\vec{v}_1, t) \; \ln[f_1(\vec{v}_1, t)] \mathrm{d}\vec{v}_1 \quad (12.15)$$

Differentiating equation (12.15) with respect to t, we have

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \int \frac{\partial f_1}{\partial t} [1 + \ln f_1] \mathrm{d}\vec{v}_1 \quad (12.16)$$

Using equation (12.16) in (12.14), we get

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \int (f_1' f_2' - f_1 f_2) 2\pi b |v_2 - v_1| [1 + \ln f_1] \mathrm{d}b \mathrm{d}\vec{v}_1 \; \mathrm{d}\vec{v}_2 \quad (12.17)$$

On interchanging $\vec{v}_1$ and $\vec{v}_2$ in the integrand, the integral remains invariant. Thus, we can write

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \int (f_1' f_2' - f_1 f_2) 2\pi b |v_1 - v_2| [1 + \ln f_2] \mathrm{d}b \mathrm{d}\vec{v}_1 \; \mathrm{d}\vec{v}_2 \quad (12.18)$$

Addition of equations (12.17) and (12.18) gives

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{1}{2} \int (f_1' f_2' - f_1 f_2) 2\pi b |v_1 - v_2| [2 + \ln(f_1 f_2)] \mathrm{d}b \; \mathrm{d}\vec{v}_1 \; \mathrm{d}\vec{v}_2 \quad (12.19)$$

As for every collision there is an inverse collision with the same impact parameter, this integral (12.19) remains invariant under the interchange of $(\vec{v}_1, \vec{v}_2)$ and $(\vec{v}'_1, \vec{v}'_2)$, and therefore, we have

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{1}{2}\int (f_1 f_2 - f'_1 f'_2) 2\pi b |v'_1 - v'_2| [2 + \ln(f'_1 f'_2)] \mathrm{d}b \; \mathrm{d}\vec{v}'_1 \; \mathrm{d}\vec{v}'_2$$

$$= \frac{1}{2}\int (f_1 f_2 - f'_1 f'_2) 2\pi b |v_1 - v_2| [2 + \ln(f'_1 f'_2)] \mathrm{d}b \; \mathrm{d}\vec{v}_1 \; \mathrm{d}\vec{v}_2 \quad (12.20)$$

where we have used the relations $\mathrm{d}\vec{v}'_1 \; \mathrm{d}\vec{v}'_2 = \mathrm{d}\vec{v}_1 \; \mathrm{d}\vec{v}_2$ and $|v'_1 - v'_2| = |v_1 - v_2|$. Addition of equations (12.19) and (12.20) gives

$$\frac{\mathrm{d}H}{\mathrm{d}t} = -\frac{1}{4}\int (f'_1 f'_2 - f_1 f_2) 2\pi b |v_1 - v_2| \ln\Big(\frac{f'_1 f'_2}{f_1 f_2}\Big) \mathrm{d}b \; \mathrm{d}\vec{v}_1 \; \mathrm{d}\vec{v}_2 \quad (12.21)$$

For all values of $f'_1 f'_2$ and $f_1 f_2$, the quantity[2]

$$(f'_1 f'_2 - f_1 f_2) \ln\Big(\frac{f'_1 f'_2}{f_1 f_2}\Big) \geq 0$$

Hence, from equation (12.21) we have

$$\frac{\mathrm{d}H}{\mathrm{d}t} \leq 0 \quad (12.22)$$

This equation (12.22) is known as the Boltzmann H-theorem. In equation (12.22), the equality sign corresponds to the equilibrium state whereas the inequality sign corresponds to the non-equilibrium state. That is

$$\frac{\mathrm{d}H}{\mathrm{d}t} = 0 \qquad \text{when} \quad f'_1 f'_2 = f_1 f_2$$

$$\frac{\mathrm{d}H}{\mathrm{d}t} < 0 \qquad \text{when} \quad f'_1 f'_2 \neq f_1 f_2$$

Moreover, for the stationary solutions, we should have $\mathrm{d}H/\mathrm{d}t = 0$.

3. Maxwell-Boltzmann distribution

As discussed for the equilibrium state, we have

$$\frac{\mathrm{d}H}{\mathrm{d}t} = 0$$

[2](i) When $f'_1 f'_2 > f_1 f_2$, we have $\ln(f'_1 f'_2 / f_1 f_2) > 0$. (ii) When $f'_1 f'_2 < f_1 f_2$, we have $\ln(f'_1 f'_2 / f_1 f_2) < 0$. (iii) When $f'_1 f'_2 = f_1 f_2$, we have $\ln(f'_1 f'_2 / f_1 f_2) = 0$.

and this occurs only when

$$f_1' f_2' = f_1 f_2 \tag{12.23}$$

On taking logarithm of equation (12.23), we have

$$\ln f_1' + \ln f_2' = \ln f_1 + \ln f_2$$

showing the conservation of f in a collision. Since energy is conserved during collision. Further, for the dilute gas, we can neglect the potential energy in comparison to the kinetic energy. Thus, we have

$$\ln f = \ln A - \beta\Big(\frac{1}{2}\ mv^2\Big)$$

It can be written as

$$f = A\ \exp\Big(-\ \frac{\beta m}{2}\ v^2\Big) \tag{12.24}$$

The constants A and β can be evaluated from the conditions

$$\int f\ \mathrm{d}\vec{v} = \frac{N}{V} = \rho \qquad\qquad \int \Big(\frac{1}{2}\ mv^2\Big) f\ \mathrm{d}\vec{v} = \frac{3}{2}\ \rho kT$$

as[3]

[3]We have

$$\rho = \int f\ \mathrm{d}\vec{v} = \int_0^\infty\int_0^\pi\int_0^{2\pi} A\ \ \exp\Big(-\ \frac{\beta m}{2}\ v^2\Big) v^2 \mathrm{d}v \sin\theta\ \mathrm{d}\theta\ \mathrm{d}\phi$$

$$= A4\pi \int_0^\infty v^2\ \exp\Big(-\ \frac{\beta m}{2}\ v^2\Big)\mathrm{d}v = A\Big(\frac{2\pi}{\beta m}\Big)^{3/2}$$

Thus,

$$A = \rho\Big(\frac{\beta m}{2\pi}\Big)^{3/2}$$

Further,

$$\frac{3}{2}\ \rho kT = \int \Big(\frac{1}{2} mv^2\Big) f\ \mathrm{d}\vec{v}$$

$$= \int_0^\infty\int_0^\pi\int_0^{2\pi} \Big(\frac{1}{2} mv^2\Big) A\ \exp\Big(-\ \frac{\beta m}{2}\ v^2\Big) v^2 \mathrm{d}v \sin\theta\ \mathrm{d}\theta\ \mathrm{d}\phi$$

$$= A2\pi m \int_0^\infty v^4\ \exp\Big(-\ \frac{\beta m}{2}\ v^2\Big)\ \mathrm{d}v = \frac{3A}{2\beta}\ \Big(\frac{2\pi}{\beta m}\Big)^{3/2}$$

Using the expression for A, we get $\beta = 1/kT$ and thus,

$$A = \rho\Big(\frac{m}{2\pi kT}\Big)^{3/2}$$

$$A = \rho\Big(\frac{m}{2\pi kT}\Big)^{3/2} \qquad\qquad \beta = \frac{1}{kT}$$

Substituting the values of A and β in equation (12.24), we get the equilibrium distribution function for a dilute gas as

$$f(v) = \rho\Big(\frac{m}{2\pi kT}\Big)^{3/2} \exp\Big(-\frac{m}{2kT}\, v^2\Big) \tag{12.25}$$

This is the Maxwell-Boltzmann velocity distribution.

3.1 Presence of an external force

In the above discussion, we have not accounted for any external forces. Let us now look into the equilibrium distribution for a dilute gas in the presence of an external force $\vec{F}$

$$\vec{F} = -\nabla_r U(r)$$

where $U(r)$ is the interaction potential between the gas and the external force. In the presence of an external force, the equilibrium distribution function becomes

$$f(r, v) = f(v)\, \exp[-U(r)/kT] \tag{12.26}$$

where $f(v)$ given by equation (12.25) is the equilibrium distribution function in absence of any external forces.

Since equation (12.26) is independent of time t, therefore $\partial f/\partial t = 0$ and the Boltzmann equation for the function $f(r, v)$ can be written as

$$\Big(\vec{v}\,.\nabla_r + \frac{\vec{F}}{m}.\nabla_v\Big) f = \exp[-U(r)/kT] \int [f_0(v_1') f_0'(v_2') - f_0(v_1) f_0(v_2)] 2\pi b v_{12}\, \mathrm{d}b\, \mathrm{d}\vec{v}_2 = 0 \tag{12.27}$$

Equation (12.26) can also be written as

$$\begin{aligned} f(r, v) &= f(v)\, \exp[-U(r)/kT] \\ &= \rho\Big(\frac{m}{2\pi kT}\Big)^{3/2} \exp\Big(-\frac{m}{2kT}\, v^2\Big) \exp[-U(r)/kT] \\ &= \rho(\vec{r})\, \Big(\frac{m}{2\pi kT}\Big)^{3/2} \exp\Big(-\frac{m}{2kT}\, v^2\Big) \end{aligned}$$

where

$$\begin{aligned} \rho(\vec{r}) &= \int f(r, v)\, \mathrm{d}\vec{v} = \int f(v)\, \exp[-U(r)/kT]\, \mathrm{d}\vec{v} \\ &= \exp[-U(r)/kT] \int f(v)\, \mathrm{d}\vec{v} = \rho\, \exp[-U(r)/kT] \end{aligned}$$

3.2 Validity of Boltzmann equation

For derivation of Boltzmann equation, we used the assumption of binary collisions (collisions between two particles) and ignored the collisions of three or more particles (mechanical assumption). Shortly after the publication of Boltzmann H-theorem, objections were raised about the mechanical assumption. The H-function satisfies the inequality condition

$$\frac{\mathrm{d}H}{\mathrm{d}t} \leq 0$$

showing the irreversibility of the Boltzmann equation. This equation is however derived from particle collisions, which are reversible in time. This situation is known as the *reversible paradox*. There is also another paradox, called the *recurrence paradox* which tells that a system can exhibit an increase as well as a decrease in the value of H, which obviously contradict the Boltzmann H-theorem.

The Boltzmann equation is strictly valid for a dilute gas where the particles are moving randomly (particle-chaos). Hence, the only real problem is to understand the precise nature of the particle-chaos and the equilibrium condition for the system.

Let us first look into the particle-chaos. Following the definition of particle-chaos, if $f(\vec{v}, t)$ is the probability density of finding a particle moving with velocity $\vec{v}$ in a gas at time t, then the probability of finding simultaneously two particles moving with velocities $\vec{v}_1$ and $\vec{v}_2$, respectively, at time t is $f(\vec{v}_1, t)\ f(\vec{v}_2, t)$. If we apply this statement for a set of particles moving with various velocities, then the probability of finding simultaneously all the particles at time t becomes $f(\vec{v}_1, t) f(\vec{v}_2, t) \ldots f(\vec{v}_N, t)$, where N is the total number of particles in the gas. This probability is obviously negligibly small. Thus, a state of the gas, for a given distribution function, may not satisfy the assumption of particle-chaos.

We can however show that when a gas is in a state of particle-chaos, the function H is at a local peak. Let us consider a gas in absence of any external forces, with an initial condition which is invariant under time-reversal. The distribution function f in this case depends only on the magnitude of the velocity $\vec{v}$ and not on its direction. Let us assume that the gas is in a state of particle-chaos which is non-Maxwellian at time $t = 0$. Then according to Boltzmann H-theorem

$$\frac{\mathrm{d}H}{\mathrm{d}t} \leq 0 \qquad \text{at} \qquad t = 0^+$$

Here, 0^+ denotes after the initial time. Let us consider another gas with the same initial conditions, but with the velocities in the reverse

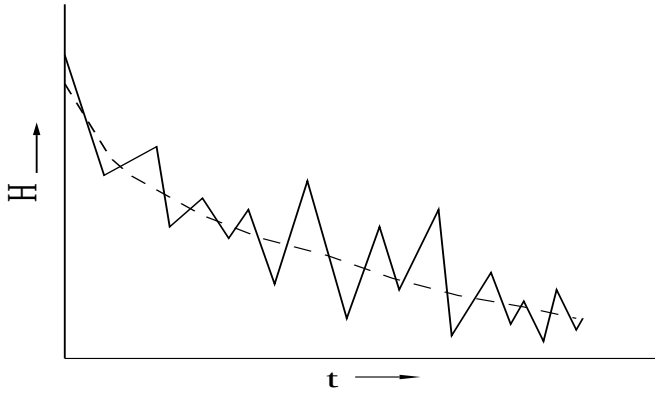


Figure 2: Variation of the function H versus time t. Solid line represents a real curve whereas the dashed line is the solution of the Boltzmann equation.

direction. The Boltzmann H-function is the same for this gas also

$$\frac{\mathrm{d}H}{\mathrm{d}t} \leq 0 \qquad \text{at} \qquad t = 0^+$$

Since the equation of motion remains invariant under time-reversal, the future of the second gas will be the past of the original gas. Hence, for the original gas, we have

$$\frac{\mathrm{d}H}{\mathrm{d}t} \leq 0 \quad \text{at} \quad t = 0^+ \qquad \frac{\mathrm{d}H}{\mathrm{d}t} \geq 0 \quad \text{at} \quad t = 0^-$$

Thus, H is at a local peak. That is,

$$\frac{\mathrm{d}H}{\mathrm{d}t} = 0 \qquad \text{at} \qquad t = 0$$

when H is not at a local peak, the gas is not in the state of particle-chaos, and the Boltzmann equation cannot be valid at all time.

It has been found that collisions can destroy the particle-chaos. Hence, the Boltzmann equation, once established to be valid, would not remain valid forever. However, for the random collisions, the distribution function remains always almost Maxwell-Boltzmann. In this case the fluctuations from equilibrium due to collisions have a short duration of the order of 10^{-11} s.

A variation of function H versus time t is shown in Figure 2, where solid line represents a real curve and the dashed line is the value obtained from the solution of the Boltzmann equation. Thus, the Boltzmann equation may be considered valid in a statistical sense. In the same sense, the Boltzmann equation provides a useful description of an approach to equilibrium.

4. Mean free path

The Boltzmann transport equation (12.13), expressing the particle collisions, is a fundamental tool to describes the basic properties of a gas. In order to understand a process that is governed by the particle collisions, we introduce the concept of the mean free path λ, which is the average distance traveled by the particles between two successive collisions. Let us consider a gas of identical particles, each of diameter d. When d is large, the probability of collisions is large and when $d \to 0$, the collision-probability tends to zero. The mean free path is an average distance traveled by a particle between two successive collisions. Suppose $\langle v \rangle$ is the average velocity of a particle making frequent collisions and τ the average time taken between two successive collisions, then the mean free path λ is

$$\lambda = \tau \ \langle v \rangle \tag{12.28}$$

For a gas in equilibrium with the normalized Maxwell distribution function

$$\hat{f}(v) = \Big(\frac{m}{2\pi kT}\Big)^{3/2} \exp\Big(-\frac{mv^2}{2kT}\Big)$$

the average velocity $\langle v \rangle$ is

$$\begin{aligned}
\langle v \rangle &= \int |v| \hat{f}(v) \ \mathrm{d}\vec{v} \\
&= \int_0^\infty \int_0^\pi \int_0^{2\pi} v \Big(\frac{m}{2\pi kT}\Big)^{3/2} \exp\Big(-\frac{mv^2}{2kT}\Big) v^2 \mathrm{d}v \sin\theta \ \mathrm{d}\theta \ \mathrm{d}\phi \\
&= 4\pi \Big(\frac{m}{2\pi kT}\Big)^{3/2} \int_0^\infty v^3 \exp\Big(-\frac{mv^2}{2kT}\Big) \ \mathrm{d}v \\
&= 4\pi \Big(\frac{m}{2\pi kT}\Big)^{3/2} \frac{1}{2} \ \Big(\frac{2kT}{m}\Big)^2 = \sqrt{\frac{8kT}{\pi m}}
\end{aligned} \tag{12.29}$$

The average collision time τ can be estimated with the help of the Boltzmann transport equation (12.13). In the equilibrium state, the number of collisions taking place per unit volume per second at a point $\vec{r}$ is

$$Z\rho = \int f_1 f_2 2\pi b v_{12} \mathrm{d}b \ \mathrm{d}\vec{v}_1 \ \mathrm{d}\vec{v}_2 \tag{12.30}$$

where ρ is the number of particles per unit volume and Z the number of collisions per particle per second, *i.e.,* the collision frequency. Hence, the average collision time τ is the reciprocal of Z. That is

$$\tau = Z^{-1} \tag{12.31}$$

Collision between two identical hard sphere particles, each of diameter d, is shown in Figure 3. The impact parameter b is

$$b = d \sin\phi$$

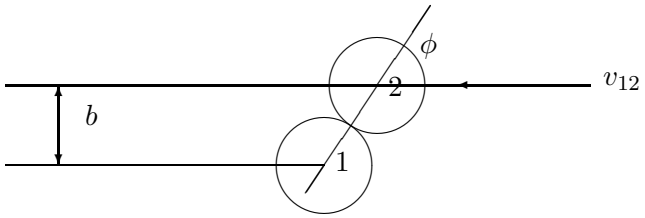


Figure 3: Collision between two identical hard sphere particles 1 and 2, each of diameter d.

Thus,

$$\mathrm{d}b = d\cos\phi \ \mathrm{d}\phi$$

and hence,

$$b \ \mathrm{d}b = d^2 \sin\phi \ \cos\phi \ \mathrm{d}\phi \tag{12.32}$$

where $0 \leq \phi \leq \pi/2$. Using equation (12.32) in (12.30), we have

$$\begin{aligned} Z\rho &= 2\pi d^2 \int f_1 f_2 v_{12} \mathrm{d}\vec{v}_1 \ \mathrm{d}\vec{v}_2 \int_0^{\pi/2} \sin\phi \ \cos\phi \ \mathrm{d}\phi \\ &= \pi d^2 \int f_1 f_2 v_{12} \mathrm{d}\vec{v}_1 \ \mathrm{d}\vec{v}_2 \end{aligned} \tag{12.33}$$

Substituting Maxwell-Boltzmann distribution function (12.25) for f_1 and f_2 in (12.33), we get

$$Z\rho = \pi d^2 \rho^2 \Big(\frac{m}{2\pi kT}\Big)^3 \int \exp\Big(-\frac{m}{2kT}(v_1^2 + v_2^2)\Big) v_{12} \mathrm{d}\vec{v}_1 \ \mathrm{d}\vec{v}_2 \tag{12.34}$$

Let us put

$$V = \frac{1}{2}(v_1 + v_2) \qquad v = (v_2 - v_1) \qquad \mathrm{d}\vec{v}_1 \ \mathrm{d}\vec{v}_2 = \mathrm{d}\vec{V} \ \mathrm{d}\vec{v}$$

then equation (12.34) becomes

$$Z = \pi d^2 \rho \Big(\frac{m}{2\pi kT}\Big)^3 \int \exp\Big[-\frac{m}{2kT}\Big(2V^2 + \frac{1}{2}v^2\Big)\Big] v \ \mathrm{d}\vec{V} \ \mathrm{d}\vec{v}$$

$$= \pi d^2 \rho \Big(\frac{m}{2\pi kT}\Big)^3 \int \exp\Big(-\frac{mV^2}{kT}\Big) \mathrm{d}\vec{V} \int v \, \exp\Big(-\frac{mv^2}{4kT}\Big) \, \mathrm{d}\vec{v}$$

$$= \pi d^2 \rho \Big(\frac{m}{2\pi kT}\Big)^3 \int_0^\infty 4\pi V^2 \exp\Big(-\frac{mV^2}{kT}\Big) \mathrm{d}V \int_0^\infty 4\pi v^3 \exp\Big(-\frac{mv^2}{4kT}\Big) \mathrm{d}v$$

$$= \pi d^2 \rho \Big(\frac{m}{2\pi kT}\Big)^3 4\pi \frac{kT}{4m} \sqrt{\frac{\pi kT}{m}} 4\pi \frac{1}{2} \Big(\frac{4kT}{m}\Big)^2 = 4d^2 \rho \sqrt{\frac{\pi kT}{m}} \qquad (12.35)$$

Form equations (12.28), (12.29), (12.31) and (12.35), we get

$$\lambda = \tau \, \langle v \rangle = Z^{-1} \sqrt{\frac{8kT}{\pi m}} = \frac{1}{4d^2 \rho} \sqrt{\frac{m}{\pi kT}} \sqrt{\frac{8kT}{\pi m}} = \Big(\pi d^2 \rho \sqrt{2}\Big)^{-1} \qquad (12.36)$$

It is interesting to note that the mean free path λ does not depend on temperature of the gas. For H_2 in the interstellar space, the density $\rho \approx 1$ molecule/cm^3 and diameter $d \approx 1\mathring{A} = 10^{-8}$ cm. Thus, the mean free path $\lambda = (3.14 \times 10^{-16} \times 1 \times \sqrt{2})^{-1} = 2 \times 10^{15}$ cm.

Exercise 1. In the interstellar space, the density of hydrogen molecule H_2 is about one molecule/cm^3. Taking the diameter of H_2 approximately 1 Å, calculate (i) average velocity of the molecule at the kinetic temperature is 100 K, (ii) mean free path of the H_2 molecules and (iii) collision frequency.

Solution: We have $\rho = 1$ molecule/cm^3, diameter $d = 1$ Å$= 10^{-8}$ cm, kinetic temperature $T = 100$ K, mass of the molecule $m = 2 \times (1.67 \times 10^{-24}) = 3.34 \times 10^{-24}$gm.

(i) Average velocity

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8 \times (1.38 \times 10^{-16}) \times 100}{3.14 \times (3.34 \times 10^{-24})}} = 1 \times 10^5 \text{ cm/s}$$

(ii) Mean free path

$$\lambda = \Big(\pi d^2 \rho \sqrt{2}\Big)^{-1} = \Big(3.14 \times 10^{-16} \times 1 \times \sqrt{2}\Big)^{-1} = 2 \times 10^{15} \text{ cm}$$

(iii) Collision frequency

$$Z = \tau^{-1} = \frac{\lambda}{\langle v \rangle} = \frac{2 \times 10^{15}}{1 \times 10^{15}} = 2 \text{ collisions per second}$$

5. Transport properties

The Boltzmann transport equation can be applied to estimate the transport properties, such as viscosity, thermal conductivity and mass diffusivity of a gas. The approach is highly mathematically involved. Hence, an approximate approach by the introduction of mean free path is often used. Let χ be any transport property of a gas associated with the motion of its constituent particles. This property is generally carried by the particles from one place to another and therefore it varies from layer to layer. Let us consider three parallel layers A, B and C, as shown in Figure 4, in a gas, such that AB = BC = λ, where λ is the mean free-path. Let the transport property in the middle plane B ($y = y_0$) be $\chi_0[= \chi(y_0)]$. Then the transport property in the plane A ($y = y_0 + \lambda\cos\theta$) is $\chi(y_0 + \lambda\cos\theta)$ which can be expressed with the help of Taylor-series as

$$\chi(y_0 + \lambda\cos\theta) = \chi_0 + \lambda\cos\theta\Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0} \tag{12.37}$$

Similarly, the transport property in the plane C ($y = y_0 - \lambda\cos\theta$) is $\chi(y_0 - \lambda\cos\theta)$ which can be expressed with the help of Taylor-series as

$$\chi(y_0 - \lambda\cos\theta) = \chi_0 - \lambda\cos\theta\Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0} \tag{12.38}$$

Let us calculate the rate at which the transport properties are transformed across a plane in the gas. Let us consider a cylinder of height v and base $\mathrm{d}s$. The volume of the cylinder is $v\ \mathrm{d}s\ \cos\theta$, where θ is the angle between normal to the surface $\mathrm{d}s$ and the direction of flow. For the distribution function f, the number of particles per unit volume in the velocity range from $\vec{v}$ to $\vec{v} + \mathrm{d}\vec{v}$ is $f\ \mathrm{d}\vec{v}$.

Thus, the number of particles in the cylinder in the velocity range from $\vec{v}$ to $\vec{v} + \mathrm{d}\vec{v}$ is

$$v\ \mathrm{d}s\ \cos\theta f\ \mathrm{d}\vec{v}$$

These particles will cross the surface area $\mathrm{d}s$ per second. Thus, the net transport of the property χ across $\mathrm{d}s$ per second is

$$\int_v \chi v\ \mathrm{d}s\ \cos\theta f\ \mathrm{d}\vec{v}$$

and the net transport of the property χ per unit area per second (which is the flux of χ) is

$$J_\chi = \int_v \chi v\ \cos\theta\ f\ \mathrm{d}\vec{v} \tag{12.39}$$

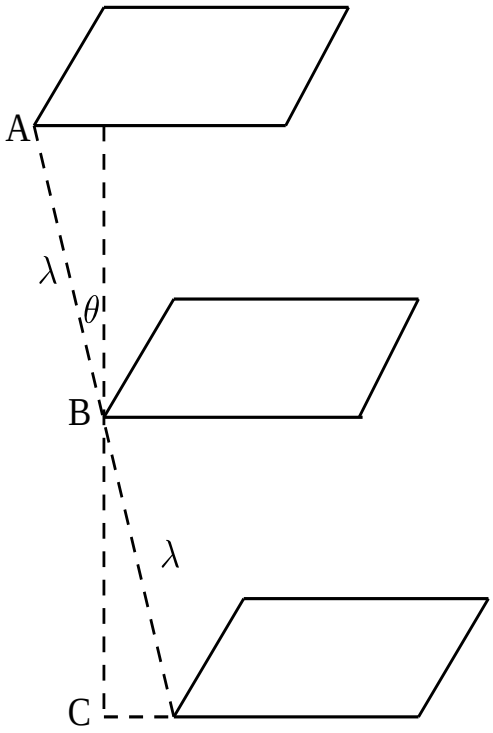


Figure 4: Three parallel layers A, B and C. The distance between two adjacent layers is $\lambda \cos\theta$.

The average velocity of a particle is[4]

$$\rho \langle v \rangle = \int v \ f(v) \ \mathrm{d} \vec{v} = \int_0^\infty \int_0^\pi \int_0^{2\pi} v^3 f(v) \ \mathrm{d}v \sin\theta \ \mathrm{d}\theta \ \mathrm{d}\phi$$

$$= 4\pi \int_0^\infty v^3 f(v) \ \mathrm{d}v \tag{12.40}$$

where ρ is the particle density. Substituting equation (12.37) in (12.39), we get

$$J_\chi^+ = \int_v \Big[\chi_0 + \lambda \cos\theta \ \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big] v \cos\theta \ f(v) \ \mathrm{d}\vec{v}$$

[4] ρ on the left side appears as $f(v)$ is not normalized and we have

$$\int f(v) \ \mathrm{d}\vec{v} = \rho$$

$$= \int_0^\infty \int_0^{\pi/2} \int_0^{2\pi} \Big[\chi_0 + \lambda \cos\theta \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big] v \cos\theta \ f(v) v^2 \mathrm{d}v \sin\theta \ \mathrm{d}\theta \ \mathrm{d}\phi$$

$$= \int_0^\infty v^3 f(v) \ \mathrm{d}v \int_0^{\pi/2} \Big[\chi_0 + \lambda \cos\theta \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big] \cos\theta \ \sin\theta \ \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi$$

$$= 2\pi \Big[\chi_0 \int_0^{\pi/2} \cos\theta \ \sin\theta \ \mathrm{d}\theta + \lambda \ \frac{\mathrm{d}\chi}{\mathrm{d}y} \int_0^{\pi/2} \cos^2\theta \ \sin\theta \ \mathrm{d}\theta\Big] \int_0^\infty v^3 f(v) \ \mathrm{d}v$$

$$= \pi \Big[\chi_0 + \frac{2}{3} \ \lambda \ \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big] \int_0^\infty v^3 f(v) \ \mathrm{d}v$$

$$= \frac{1}{4} \ \rho \ \langle v \rangle \Big[\chi_0 + \frac{2}{3} \ \lambda \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big] \tag{12.41}$$

Since we are not accounting for the particles in the reverse direction, the angle here θ varies between 0 and $\pi/2$. Similarly, substituting equation (12.38) in (12.39), we get

$$J_\chi^- = \int_v \Big[\chi_0 - \lambda \cos\theta \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big] v \cos\theta \ f(v) \ \mathrm{d}\vec{v}$$

$$= \int_0^\infty \int_0^{\pi/2} \int_0^{2\pi} \Big[\chi_0 - \lambda \cos\theta \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big] v \cos\theta \ f(v) v^2 \mathrm{d}v \sin\theta \ \mathrm{d}\theta \mathrm{d}\phi$$

$$= \int_0^\infty v^3 f(v) \ \mathrm{d}v \int_0^{\pi/2} \Big[\chi_0 - \lambda \cos\theta \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big] \cos\theta \ \sin\theta \ \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi$$

$$= 2\pi \Big[\chi_0 \int_0^{\pi/2} \cos\theta \ \sin\theta \ \mathrm{d}\theta - \lambda \ \frac{\mathrm{d}\chi}{\mathrm{d}y} \int_0^{\pi/2} \cos^2\theta \ \sin\theta \ \mathrm{d}\theta\Big] \int_0^\infty v^3 f(v) \mathrm{d}v$$

$$= \frac{1}{4} \ \rho \ \langle v \rangle \Big[\chi_0 - \frac{2}{3} \ \lambda \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big] \tag{12.42}$$

Thus, the net flux of χ, J_χ crossing the surface $y = y_0$ from C to A is

$$J_\chi = J_\chi^- - J_\chi^+$$

$$= \frac{1}{4} \ \rho \ \langle v \rangle \Big[\chi_0 - \frac{2}{3} \ \lambda \ \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big] - \frac{1}{4} \ \rho \ \langle v \rangle \Big[\chi_0 + \frac{2}{3} \ \lambda \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0}\Big]$$

$$= -\frac{1}{3} \ \rho \ \langle v \rangle \ \lambda \Big(\frac{\mathrm{d}\chi}{\mathrm{d}y}\Big)_{y_0} \tag{12.43}$$

Now we shall apply this theory of transport properties to explain some properties of a dilute gas. This theory is also known as the theory of mean free-path.

5.1 Viscosity

Let us apply the above theory to understand the viscosity of a gas. In a gas, we can consider various layers which are in relative motion due to its viscosity. Owing to the relative motion between various layers of a gas, the layers apply forces on one another. The force per unit area of contact is

$$F = -\eta \frac{\mathrm{d}u}{\mathrm{d}y} \tag{12.44}$$

where η is the coefficient of viscosity and $\mathrm{d}u/\mathrm{d}y$ the velocity gradient. In the case of viscosity, the transport property is the momentum, *i.e.,*

$$\chi = mu \tag{12.45}$$

Using equation (12.45) in (12.43), we get the rate of transfer of momentum

$$J_m = -\frac{1}{3}\,\rho u\lambda \left(\frac{\mathrm{d}mu}{\mathrm{d}y}\right)_{y_0} = -\frac{1}{3}\,\rho mu\lambda \left(\frac{\mathrm{d}u}{\mathrm{d}y}\right)_{y_0} \tag{12.46}$$

The momentum flux J_m, which is the rate of transfer of momentum across an area, is equal to the force exerted on the gas to sustain equilibrium. Thus, from equations (12.44) and (12.46), we have

$$F = J_m \qquad \text{or} \qquad -\eta \frac{\mathrm{d}u}{\mathrm{d}y} = -\frac{1}{3}\,\rho\, mu\lambda \frac{\mathrm{d}u}{\mathrm{d}y}$$

It gives

$$\eta = \frac{1}{3}\,\rho mu\lambda \tag{12.47}$$

Using equation (12.36) in (12.47), we have

$$\eta = \frac{1}{3\sqrt{2}}\,\frac{mu}{\pi d^2} \tag{12.48}$$

It shows that η depends on mass and diameter of particles and is independent of the density.

5.2 Thermal conductivity

Let us now apply the above theory to understand thermal conductivity of a gas. In a gas, temperature (thermal energy) varies from layer to layer. Let $(\mathrm{d}T/\mathrm{d}y)_{y_0}$ be the temperature gradient and K the thermal conductivity of the gas, then the flow of heat per unit area per second is

$$Q_{y_0} = -K \left(\frac{\mathrm{d}T}{\mathrm{d}y}\right)_{y_0} \tag{12.49}$$

In the case of thermal conductivity, the transport property is the thermal energy. That is

$$\chi = \langle \varepsilon \rangle \tag{12.50}$$

where ε is average energy of particles of the gas. Using equation (12.50) in (12.43), we get the rate of flow of energy as

$$J_{ene} = -\frac{1}{3}\, \rho\, \langle v \rangle\, \lambda \Big(\frac{\mathrm{d}\langle \varepsilon \rangle}{\mathrm{d}y}\Big)_{y_0} \tag{12.51}$$

Specific heat at constant volume c_V is

$$mc_V = \Big(\frac{\mathrm{d}\langle \varepsilon \rangle}{\mathrm{d}T}\Big)_V = \Big(\frac{\mathrm{d}\langle \varepsilon \rangle}{\mathrm{d}y}\Big)_{y_0} \Big(\frac{\mathrm{d}y}{\mathrm{d}T}\Big)_{y_0}$$

where m is the mass of a particle. Thus, we have

$$\Big(\frac{\mathrm{d}\langle \varepsilon \rangle}{\mathrm{d}y}\Big)_{y_0} = mc_V \Big(\frac{\mathrm{d}T}{\mathrm{d}y}\Big)_{y_0}$$

and

$$J_{ene} = -\frac{1}{3}\, \rho\, \langle v \rangle\, \lambda m\, c_V \left(\frac{\mathrm{d}T}{\mathrm{d}y}\right)_{y_0} \tag{12.52}$$

Thus, from equations (12.49) and (12.52), we have

$$Q_{y_0} = J_{ene} \qquad \text{or} \qquad -K \left(\frac{\mathrm{d}T}{\mathrm{d}y}\right)_{y_0} = -\frac{1}{3}\, \rho\, \langle v \rangle\, \lambda m c_V \Big(\frac{\mathrm{d}T}{\mathrm{d}y}\Big)_{y_0}$$

It gives

$$K = \frac{1}{3}\, \rho\, \langle v \rangle\, \lambda m c_V \tag{12.53}$$

Using equation (12.36) in (12.53), we have

$$K = \frac{1}{3\sqrt{2}}\, \frac{m\, \langle v \rangle\, c_V}{\pi d^2} \tag{12.54}$$

It shows that K depends on mass and diameter of particles and is independent of the density.

5.3 Diffusion

Consider a gas having constant temperature and pressure. A gas can be considered made up of various horizontal layers. Let us assume that the concentration in a horizontal layer is constant. The concentration of particles in the gas varies from layer to layer in the vertical direction. Let $(\mathrm{d}\rho/\mathrm{d}y)_{y_0}$ be the density gradient and D the coefficient of diffusion of the gas, then the number of particles crossing unit area of the horizontal plane per second (*i.e.,* the mass flux) is

$$J_m = -D\Big(\frac{\mathrm{d}\rho}{\mathrm{d}y}\Big)_{y_0} \tag{12.55}$$

In order to understand the phenomenon of diffusion on the basis of mean free path, let us assume that two gases are placed one above the other. Because of their molecular motion, these two gases mix with each other even against the gravity. Finally, they reach a steady state when the particle concentrations of the two gases in any horizontal plain attain steady values. However, the particle concentration varies in the vertical direction.

Let ρ_1 and ρ_2 be the number densities of two components. Since the number density ρ of the mixture must be equal to the sum of the components, we have

$$\rho_1 + \rho_2 = \rho = \text{constant}$$

Thus, the concentration gradients must obey the relation

$$\frac{\mathrm{d}\rho_1}{\mathrm{d}y} + \frac{\mathrm{d}\rho_2}{\mathrm{d}y} = 0 \qquad \text{or} \qquad \frac{\mathrm{d}\rho_1}{\mathrm{d}y} = -\frac{\mathrm{d}\rho_2}{\mathrm{d}y} = \alpha \tag{12.56}$$

where α is a constant. Form equation (12.56), we have

$$\rho_1 = A_1 + \alpha y \qquad \text{and} \qquad \rho_2 = A_2 - \alpha y$$

where A_1 and A_2 are constants. In the case of diffusion, transport property is the number density, and is similar to equation (12.43), we can write

$$J_{\rho_1} = -\frac{1}{3}\,\langle v_1\rangle\,\lambda_1\Big(\frac{\mathrm{d}\rho_1}{\mathrm{d}y}\Big)_{y_0} = -\frac{1}{3}\,\alpha\,\langle v_1\rangle\lambda_1 \tag{12.57}$$

and

$$J_{\rho_2} = -\frac{1}{3}\,\langle v_2\rangle\,\lambda_2\Big(\frac{\mathrm{d}\rho_2}{\mathrm{d}y}\Big)_{y_0} = \frac{1}{3}\,\alpha\,\langle v_2\rangle\,\lambda_2 \tag{12.58}$$

Since the molecular fluxes balance each other, we have

$$J_{\rho_1} = -J_{\rho_2} \qquad \text{or} \qquad -\frac{1}{3}\,\alpha\,\langle v_1\rangle\,\lambda_1 = -\frac{1}{3}\,\alpha\,\langle v_2\rangle\,\lambda_2$$

It gives

$$\langle v_1 \rangle \ \lambda_1 = \langle v_2 \rangle \ \lambda_2 \tag{12.59}$$

Equation (12.55) can be written as

$$J_{\rho_1} = -D_{12} \left(\frac{\mathrm{d}\rho_1}{\mathrm{d}y} \right)_{y_0} = -D_{12}\alpha \tag{12.60}$$

and

$$J_{\rho_2} = -D_{21} \left(\frac{\mathrm{d}\rho_2}{\mathrm{d}y} \right)_{y_0} = D_{21} \ \alpha \tag{12.61}$$

From equations (12.57) and (12.60), we have

$$-D_{12}\alpha = -\frac{1}{3} \ \alpha \ \langle v_1 \rangle \lambda_1 \qquad \text{or} \qquad D_{12} = \frac{1}{3} \ \langle v_1 \rangle \lambda_1 \tag{12.62}$$

From equations (12.57) and (12.61), we have

$$D_{21}\alpha = \frac{1}{3} \ \alpha \ \langle v_2 \rangle \lambda_2 \qquad \text{or} \qquad D_{21} = \frac{1}{3} \ \langle v_2 \rangle \lambda_2 \tag{12.63}$$

From equations (12.59), (12.62) and (12.63), we have gives

$$D_{12} = D_{21} \tag{12.64}$$

This equation (12.64) is accurate only when two components of the gas are nearly identical. In this case, the diffusion coefficients D_{12} and D_{21} approach to a common value D_{11}, called the coefficient of self-diffusion.

In general, $J_{\rho_1} \neq -J_{\rho_2}$ and there is a tendency for a net transfer of particles in an upward direction. It leads to a pressure gradient in the gas. Since the pressure must remain constant throughout the gas, this tendency is balanced by slow mass motion with a mass velocity w in the vertically downward direction. This velocity is evidently such that it establishes the equality of transport in both directions. Then the actual transfers in the two directions are

$$T_1 = J_{\rho_1} + w\rho_1 \qquad T_2 = J_{\rho_2} + w\rho_2 \tag{12.65}$$

These fluxes must balance each other, *i.e.,*

$$T_1 = -T_2$$

Using equation (12.65) in this equation, we get

$$J_{\rho_1} + w\rho_1 = -(J_{\rho_2} + w\rho_2) \qquad \text{or} \qquad w = -\frac{J_{\rho_1} + J_{\rho_2}}{\rho_1 + \rho_2}$$

Using the value of w in equation (12.65), we get

$$T_1 = J_{\rho_1} - \frac{J_{\rho_1} + J_{\rho_2}}{\rho_1 + \rho_2}\ \rho_1 = \frac{J_{\rho_1}\rho_2 - J_{\rho_2}\rho_1}{\rho_1 + \rho_2} \tag{12.66}$$

Using equations (12.57) and (12.58) along with (12.56) in (12.67), we get

$$T_1 = -\frac{1}{3}\ \frac{\langle v_1\rangle\ \lambda_1\rho_2 + \langle v_2\rangle\ \lambda_2\rho_1}{\rho_1 + \rho_2}\ \Big(\frac{\mathrm{d}\rho_1}{\mathrm{d}y}\Big) \tag{12.67}$$

Using the definition

$$T_1 = -D_{12}\ \Big(\frac{\mathrm{d}\rho_1}{\mathrm{d}y}\Big)_{y_0}$$

we get

$$D_{12} = \frac{1}{3}\ \frac{\langle v_1\rangle\ \lambda_1\rho_2 + \langle v_2\rangle\ \lambda_2\rho_1}{\rho_1 + \rho_2} \tag{12.68}$$

Equation (12.68) is generally known as Mayer's formula for the coefficient of diffusion of one gas into another. The coefficient D_{12} is often called the coefficient of mutual diffusion. When the molecules of two gases are approximately identical in size and mass, we can assume $\lambda_1 = \lambda_2$ and $\langle v_1\rangle = \langle v_2\rangle$ and the equation (12.68) reduces to (12.64). Thus, we have

$$D_{11} = \frac{1}{3}\ \langle v_1\rangle\ \lambda_1 = \eta/\rho m$$

This relation however does not agree with the experimental results. For getting the agreement, we write

$$D_{11} = \varepsilon\eta/\rho m$$

where $\varepsilon = 1.2$ for elastic spheres.

6. Problems and questions

1. Derive the expression for loss coefficient in the Boltzmann transport equation.

2. Derive the expression for gain coefficient in the Boltzmann transport equation.

3. Derive the Boltzmann distribution function.

4. Derive the Boltzmann transport equation and discuss its validity.

5. Show that the mean free-path does not depend on the temperature of the gas.

6. Describe the phenomenon of viscosity with the help of the theory of mean free-path.

7. Describe the phenomenon of thermal conductivity with the help of the theory of mean free-path.

8. Describe the phenomenon of diffusion with the help of the theory of mean free-path.

9. Derive an expression for Maxwell-Boltzmann velocity distribution for a dilute gas in absence of any external forces. Modify the distribution function for an external force $\vec{F}$, defined as $\vec{F} = -\nabla_r U(r)$, and show that the present distribution function satisfies the Boltzmann equation.

10. What do you understand by mean free path in a gas. Derive expression for it.

11. State and prove Boltzmann H-theorem.

12. Derive an expression for distribution function for an ideal gas in equilibrium.

13. For an ideal gas in absence of any external fields, show that the equilibrium distribution function is

$$f(v) = \rho\Big(\frac{m}{2\pi kT}\Big)^{3/2} \exp\Big(-\frac{mv^2}{2kT}\Big)$$

14. For an ideal gas in presence of an external field $\vec{F}$, defined as $\vec{F} = -\nabla_r U(r)$, show that the equilibrium distribution function is

$$f(v) = \rho\Big(\frac{m}{2\pi kT}\Big)^{3/2} \exp\Big(-\frac{mv^2}{2kT} - \frac{U}{kT}\Big)$$

15. Write notes on the following

    (i) Boltzmann transport equation

    (ii) Boltzmann H-theorem

    (iii) Maxwell-Boltzmann velocity distribution

(iv) Validity of Boltzmann equation

(v) Mean free path

(vi) Viscosity of a gas

(vii) Thermal conductivity of a gas

(viii) Diffusion in a gas

XIII. Dynamical Theory of Gases

In this chapter, we intend to discuss about the dynamical properties of fluids. Thermodynamical quantities of a system have some random fluctuations from their mean values. These random fluctuations play important role in non-equilibrium statistical mechanics and provide a natural framework for understanding some physical phenomena like Brownian motion. The mechanism of Brownian motion tells how a physical system, which is not in equilibrium, ultimately comes to an equilibrium state. Study of fluctuations also requires the concept of correlation functions, which play important role in providing the dissipative properties of a system.

1. Fluctuations and thermodynamic properties

As we discussed earlier, what we measure is the mean value of a physical quantity. In fact, a physical quantity f, in general, differs from its mean value $\langle f \rangle$. The fluctuation Δf of the physical quantity f from its mean value $\langle f \rangle$ is expressed as

$$\Delta f = f - \langle f \rangle$$

Value of Δf varies between negative and positive values. In a system, a thermodynamical quantity has small random fluctuations from its mean values. Now, we want to calculate the mean square fluctuations of fundamental thermodynamical quantities of the system. Let us consider a physical system A embedded in a reservoir B as shown in Figure 1. Suppose E_1 and E_2 are energies, and V_1 and V_2 the volumes of the system and reservoir, respectively. If E and V are the total energy and volume, respectively, of the composite system (A + B), then we have

$$E = E_1 + E_2 = \text{constant} \qquad \text{and} \qquad V = V_1 + V_2 = \text{constant}$$

Since A and B can exchange energy, they will be in the thermal equilibrium (temperatures will be equal; $T_1 = T_2 = T$). Further, A and B can

exchange volume, they will be in the mechanical equilibrium (pressures will be equal; $P_1 = P_2 = P$). Thus, we have

$$\mathrm{d}E_1 + \mathrm{d}E_2 = 0 \qquad \text{and} \qquad \mathrm{d}V_1 + \mathrm{d}V_2 = 0 \tag{13.1}$$

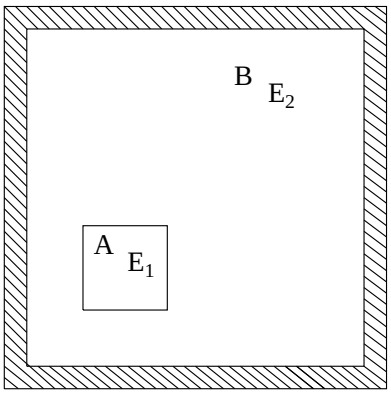


Figure 1: System A is embedded in a reservoir B at equilibrium temperature T and pressure P.

In equilibrium, let the system (A + B) has common temperature T and pressure P. Suppose $S(E, V)$ is the actual entropy of the system. If S_0 is the equilibrium entropy of the system as a function of its mean energy $\langle E \rangle$ and mean volume $\langle V \rangle$. The fluctuation of entropy from its equilibrium value S_0 is

$$\Delta S = \int_0^f \mathrm{d}S = S - S_0$$

The lower and upper limits of the integral represent the initial and final states of the system. Let S_1 and S_2 are entropies of the system and reservoir, respectively. Total entropy S of the system (A + B) is

$$S = S_1 + S_2$$

Thus, the fluctuations are[1]

$$\Delta S = \Delta S_1 + \Delta S_2 = \Delta S_1 + \int_0^f \mathrm{d}S_2$$

[1]We have $S_2 = S_2(E_2, V_2)$ and therefore,

$$\mathrm{d}S_2 = \frac{\partial S_2}{\partial E_2}\,\mathrm{d}E_2 + \frac{\partial S_2}{\partial V_2}\,\mathrm{d}V_2 = \frac{1}{T_2}\,\mathrm{d}E_2 + \frac{P_2}{T_2}\,\mathrm{d}V_2 = \frac{\mathrm{d}E_2 + P_2\,\mathrm{d}V_2}{T_2}$$

$$= \Delta S_1 + \int_0^f \frac{\mathrm{d}E_2 + P_2\ \mathrm{d}V_2}{T_2} \tag{13.2}$$

Using equation (13.1) in (13.2) and for the fact that the system (A + B) has a common temperature T and pressure P, we have

$$\Delta S = \Delta S_1 - \int_0^f \frac{\mathrm{d}E_1 + P\mathrm{d}V_1}{T} = \Delta S_1 - \frac{1}{T}\int_0^f \mathrm{d}E_1 - \frac{P}{T}\int_0^f \mathrm{d}V_1$$

$$= \Delta S_1 - \frac{1}{T}\ \Delta E_1 - \frac{P}{T}\ \Delta V_1 = \Delta S_1 - \frac{\Delta E_1 + P\Delta V_1}{T}$$

The probability ρ that the fluctuation may occur in the system is

$$\rho \propto \exp\Big(\frac{\Delta S}{k}\Big) = \exp\Big[-\frac{(\Delta E_1 - T\Delta S_1 + P\Delta V_1)}{kT}\Big]$$

It shows that the probability distribution law does not depend on the nature of the reservoir. As the reservoir does not come in the picture any more and all the parameters are for the system of interest, for convenience, we may drop the suffix 1 from the physical quantities for further discussion, so that we have

$$\rho \propto \exp\Big[-\frac{(\Delta E - T\Delta S + P\Delta V)}{kT}\Big] \tag{13.3}$$

Equation (13.3) is applicable to the fluctuations in any physical quantity.

Considering energy E as a function of V as well as S, for fluctuation in energy ΔE, a Taylor series expansion about the equilibrium value $(\Delta E)_0 = 0$ can be written as

$$\Delta E = \Big(\frac{\partial E}{\partial S}\Big)_0 \Delta S + \Big(\frac{\partial E}{\partial V}\Big)_0 \Delta V + \frac{1}{2}\Big(\frac{\partial^2 E}{\partial S^2}\Big)_0 (\Delta S)^2$$

$$+\Big(\frac{\partial^2 E}{\partial S \partial V}\Big)_0 \Delta S \Delta V + \frac{1}{2}\Big(\frac{\partial^2 E}{\partial V^2}\Big)_0 (\Delta V)^2$$

Here, higher order terms are neglected. Using

$$T = \Big(\frac{\partial E}{\partial S}\Big)_0 \qquad \text{and} \qquad P = -\Big(\frac{\partial E}{\partial V}\Big)_0$$

we have

$$\Delta E - T\Delta S + P\Delta V = \frac{1}{2}\Big[\Big(\frac{\partial^2 E}{\partial S^2}\Big)_0 (\Delta S)^2 + \Big(\frac{\partial^2 E}{\partial S \partial V}\Big)_0 \Delta S \Delta V\Big]$$

$$+\frac{1}{2}\Big[\Big(\frac{\partial^2 E}{\partial S \partial V}\Big)_0 \Delta S \Delta V + \Big(\frac{\partial^2 E}{\partial V^2}\Big)_0 (\Delta V)^2\Big]$$

$$= \frac{1}{2}\Big[\Big(\frac{\partial}{\partial S}\Big(\frac{\partial E}{\partial S}\Big)\Big)_0 \Delta S + \Big(\frac{\partial}{\partial V}\Big(\frac{\partial E}{\partial S}\Big)\Big)_0 \Delta V\Big]\Delta S$$

$$+\frac{1}{2}\Big[\Big(\frac{\partial}{\partial S}\Big(\frac{\partial E}{\partial V}\Big)\Big)_0 \Delta S + \Big(\frac{\partial}{\partial V}\Big(\frac{\partial E}{\partial V}\Big)\Big)_0 \Delta V\Big]\Delta V$$

$$= \frac{1}{2}\Big[\Big(\frac{\partial T}{\partial S}\Big)_0 \Delta S + \Big(\frac{\partial T}{\partial V}\Big)_0 \Delta V\Big]\Delta S - \frac{1}{2}\Big[\Big(\frac{\partial P}{\partial S}\Big)_0 \Delta S + \Big(\frac{\partial P}{\partial V}\Big)_0 \Delta V\Big]\Delta V$$

Using

$$\Delta T = \frac{\partial T}{\partial S}\,\Delta S + \frac{\partial T}{\partial V}\,\Delta V \qquad \text{and} \qquad \Delta P = \frac{\partial P}{\partial S}\,\Delta S + \frac{\partial P}{\partial V}\,\Delta V$$

we get

$$\Delta E - T\Delta S + P\Delta V = \frac{1}{2}\Big[\Delta T \Delta S - \Delta P \Delta V\Big] \tag{13.4}$$

Using equation (13.4) in (13.3), we get the fluctuation probability as

$$\rho \propto \exp\Big[\frac{\Delta P \Delta V - \Delta T \Delta S}{2kT}\Big] \tag{13.5}$$

This expression can be used to calculate the fluctuations of various thermodynamical quantities.

1.1 Fluctuation in entropy

Considering the entropy $S(T, V)$ as a function of independent variables T and V, the fluctuation in entropy can be expressed as

$$\Delta S = \Big(\frac{\partial S}{\partial T}\Big)_V \Delta T + \Big(\frac{\partial S}{\partial V}\Big)_T \Delta V$$

Using the relations

$$c_V = T\Big(\frac{\partial S}{\partial T}\Big)_V \qquad \text{and} \qquad \Big(\frac{\partial S}{\partial V}\Big)_T = \Big(\frac{\partial P}{\partial T}\Big)_V$$

we get

$$\Delta S = \frac{c_V}{T}\Delta T + \Big(\frac{\partial P}{\partial T}\Big)_V \Delta V \tag{13.6}$$

Here, c_V is specific heat at constant volume.

1.2 Fluctuation in pressure

Considering the pressure $P(T, V)$ as function of independent variables T and V, the fluctuation in pressure can be expressed as

$$\Delta P = \Big(\frac{\partial P}{\partial T}\Big)_V \Delta T + \Big(\frac{\partial P}{\partial V}\Big)_T \Delta V$$

Defining the isothermal compressibility

$$K_T = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_T \qquad \text{so that} \qquad \Big(\frac{\partial V}{\partial P}\Big)_T = -\frac{1}{K_T V}$$

Therefore, we have

$$\Delta P = \Big(\frac{\partial P}{\partial T}\Big)_V \Delta T - \frac{1}{K_T V}\,\Delta V \tag{13.7}$$

Using equations (13.6) and (13.7) in (13.5), we get

$$\rho \propto \exp\Big[\frac{\Delta V}{2kT}\Big\{\Big(\frac{\partial P}{\partial T}\Big)_V \Delta T - \frac{1}{K_T V}\Delta V\Big\} - \frac{\Delta T}{2kT}\Big\{\frac{c_V}{T}\Delta T + \Big(\frac{\partial P}{\partial T}\Big)_V \Delta V\Big\}\Big]$$

$$= \exp\Big[-\frac{c_V}{2kT^2}\Big(\Delta T\Big)^2 - \frac{1}{2kTK_T V}\Big(\Delta V\Big)^2\Big] \tag{13.8}$$

This relation shows that the fluctuations of T and V are statistically independent as the term $(\Delta T\ \Delta V)$ is absent here. Each term in equation (13.8) represents a Gaussian distribution as

$$f_T = A_T\ \exp\Big[-\frac{c_V(\Delta T)^2}{2kT^2}\Big] \qquad \text{and} \qquad f_V = A_V\ \exp\Big[-\frac{(\Delta V)^2}{2kTK_T V}\Big]$$

(i) For the distribution f_T, the average of $(\Delta T)^2$ is[2]

$$\langle(\Delta T)^2\rangle = \frac{\int_0^\infty (\Delta T)^2 A_T\ \exp\Big[-c_V(\Delta T)^2/2kT^2\Big]\mathrm{d}(\Delta T)}{\int_0^\infty A_T\ \exp\Big[-c_V(\Delta T)^2/2kT^2\Big]\mathrm{d}(\Delta T)} = \frac{kT^2}{c_V}$$

[2]Let us consider the equation

$$\big\langle\Delta^2\big\rangle = \frac{\int_0^\infty \Delta^2 A\ \exp(-\Delta^2/a^2)\mathrm{d}\Delta}{\int_0^\infty A_T\ \exp(-\Delta^2/a^2)\mathrm{d}\Delta}$$

Let

$$\Delta = a\sqrt{t} \qquad \text{so that} \qquad \mathrm{d}\Delta = \frac{a}{2\sqrt{t}}\ \mathrm{d}t$$

Thus, we have

$$\big\langle\Delta^2\big\rangle = \frac{a^2\int_0^\infty t^{1/2}\ \exp(-t)\ \mathrm{d}t}{\int_0^\infty t^{-1/2}\ \exp(-t)\ \mathrm{d}t} = \frac{a^2\Gamma(3/2)}{\Gamma(1/2)} = \frac{a^2}{2}$$

(ii) For the distribution f_V, the average of $(\Delta V)^2$ is

$$\langle(\Delta V)^2\rangle = \frac{\int_0^\infty (\Delta V)^2 A_V \exp\Big[-(\Delta V)^2/2kTK_TV\Big]\mathrm{d}(\Delta V)}{\int_0^\infty A_V \exp\Big[-(\Delta V)^2/2kTK_TV\Big]\mathrm{d}(\Delta V)} = kTK_TV$$

1.3 Fluctuation in volume

Considering the volume $V(S,P)$ as a function of independent variables S and P, the fluctuation in volume can be expressed as

$$\Delta V = \Big(\frac{\partial V}{\partial P}\Big)_S \Delta P + \Big(\frac{\partial V}{\partial S}\Big)_P \Delta S$$

Using the relations

$$K_S = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_S \qquad \text{and} \qquad \Big(\frac{\partial V}{\partial S}\Big)_P = \Big(\frac{\partial T}{\partial P}\Big)_S$$

we get

$$\Delta V = -K_S V \Delta P + \Big(\frac{\partial T}{\partial P}\Big)_S \Delta S \tag{13.9}$$

1.4 Fluctuation in temperature

Considering the temperature $T(S,P)$ as a function of independent variables S and P, the fluctuation in temperature can be expressed as

$$\Delta T = \Big(\frac{\partial T}{\partial P}\Big)_S \Delta P + \Big(\frac{\partial T}{\partial S}\Big)_P \Delta S$$

Defining specific heat at constant pressure

$$c_P = T\Big(\frac{\partial S}{\partial T}\Big)_P$$

we have

$$\Delta T = \Big(\frac{\partial T}{\partial P}\Big)_S \Delta P + \frac{T}{c_P}\Delta S \tag{13.10}$$

Using equations (13.9) and (13.10) in (13.5), we get

$$\rho \propto \exp\Big[\frac{\Delta P}{2kT}\Big\{-K_SV\Delta P + \Big(\frac{\partial T}{\partial P}\Big)_S \Delta S\Big\} - \frac{\Delta S}{2kT}\Big\{\Big(\frac{\partial T}{\partial P}\Big)_S \Delta P + \frac{T}{c_P}\Delta S\Big\}\Big]$$

$$= \exp\Big[-\frac{K_SV}{2kT}(\Delta P)^2 - \frac{1}{2kc_P}(\Delta S)^2\Big] \tag{13.11}$$

This relation shows that the fluctuations of S and P are statistically independent because the term $(\Delta S\ \Delta P)$ is absent here. Each term in equation (13.11) represents a Gaussian distribution as

$$f_S = A_S \exp\Big[-\frac{(\Delta S)^2}{2kc_P}\Big] \qquad \text{and} \qquad f_P = A_P \exp\Big[-\frac{K_S V(\Delta P)^2}{2kT}\Big]$$

Thus, we get the averages

$$\langle(\Delta P)^2\rangle = \frac{kT}{K_S V} \qquad \text{and} \qquad \langle(\Delta S)^2\rangle = kc_P$$

1.5 Fluctuation in total energy

Considering the total energy $U(T, V)$ as a function of independent variables T and V, the fluctuation in total energy can be expressed as

$$\Delta U = \Big(\frac{\partial U}{\partial T}\Big)_V \Delta T + \Big(\frac{\partial U}{\partial V}\Big)_T \Delta V$$

Squaring and averaging, we have

$$\langle(\Delta U)^2\rangle = \Big\langle \Big[\Big(\frac{\partial U}{\partial T}\Big)_V\Big]^2 (\Delta T)^2 + \Big[\Big(\frac{\partial U}{\partial V}\Big)_T\Big]^2 (\Delta V)^2$$

$$+2\Big(\frac{\partial U}{\partial T}\Big)_V \Big(\frac{\partial U}{\partial V}\Big)_T \Delta T\ \Delta V\Big\rangle$$

$$= \Big[\Big(\frac{\partial U}{\partial T}\Big)_V\Big]^2 \langle(\Delta T)^2\rangle + \Big[\Big(\frac{\partial U}{\partial V}\Big)_T\Big]^2 \langle(\Delta V)^2\rangle$$

$$+2\Big(\frac{\partial U}{\partial T}\Big)_V \Big(\frac{\partial U}{\partial V}\Big)_T \langle\Delta T\ \Delta V\rangle$$

Since T and V are independent variables, we have $\langle\Delta T\ \Delta V\rangle = 0$. Using the values of $\langle(\Delta T)^2\rangle$ and $\langle(\Delta V)^2\rangle$, we have

$$\langle(\Delta U)^2\rangle = c_V^2\ \frac{kT^2}{c_V} + \Big[\Big(\frac{\partial U}{\partial V}\Big)_T\Big]^2\ kTK_T V$$

$$= c_V kT^2 + \Big[\Big(\frac{\partial U}{\partial V}\Big)_T\Big]^2 kTK_T V$$

Now,[3]

$$\Big(\frac{\partial U}{\partial V}\Big)_T = \Big(\frac{\partial U}{\partial N}\frac{\partial N}{\partial V}\Big)_T = \Big(\frac{\partial U}{\partial N}\frac{N}{V}\Big)_T$$

Thus, we have

$$\langle(\Delta U)^2\rangle = c_V kT^2 + kTK_T V\ \Big(\frac{N}{V}\Big)^2\Big[\Big(\frac{\partial U}{\partial N}\Big)_T\Big]^2$$

$$= c_V kT^2 + kTK_T\ \frac{N^2}{V}\Big[\Big(\frac{\partial U}{\partial N}\Big)_T\Big]^2 \tag{13.12}$$

Equation(**??**) gives fluctuation in volume of the system having a fixed number N of particles. Thus, the volume fluctuation per particle can be obtained as

$$\langle(\Delta(V/N))^2\rangle = \frac{kTV}{N^2}\ K_T \tag{13.13}$$

When V is constant, we have

$$\Delta(V/N) = -\frac{V}{N^2}\ \Delta N \tag{13.14}$$

Using equation (13.14) in (13.13), we have

$$\frac{V^2}{N^4}\ \langle(\Delta N)^2\rangle = \frac{kTV}{N^2}K_T \qquad \text{or} \qquad \frac{kTN^2}{V}K_T = \langle(\Delta N)^2\rangle \tag{13.15}$$

Using equation (13.15) in (13.12), we have

$$\langle(\Delta U)^2\rangle = c_V kT^2 + \langle(\Delta N)^2\rangle\ \Big[\Big(\frac{\partial U}{\partial N}\Big)_T\Big]^2$$

This formula is applicable to a substance with constant volume and fluctuating number of particles.

2. Brownian motion

If we look for the motions of fine particles suspended in a fluid. These particles move continuously with high speed in a random manner throughout the fluid. A part of the typical motion of a fine particle suspended in a fluid is shown in Figure 2. Such a motion of particles is known as

[3]Ideal gas equation is

$$PV = NkT \qquad P = \Big(\frac{\partial N}{\partial V}\Big)_T kT \qquad \frac{NkT}{V} = \Big(\frac{\partial N}{\partial V}\Big)_T kT \qquad \Big(\frac{\partial N}{\partial V}\Big)_T = \frac{N}{V}$$

the Brownian motion and the particles are referred to as the Brownian particles. Theoretical analysis of the Brownian motion was first given by Einstein on the basis of the random walk. He predicted that Brownian motion was due to fluctuations in molecular constants and analyzed the motion of the particles as equivalent to the diffusion of particles through the fluid. Let $\rho(\vec{r},t)$ be the number density and $\vec{J}(\vec{r},t)$ the current density of particles moving in the fluid. For the diffusion of particles, the Fick's law states

$$\vec{J}(\vec{r},t) = -D\ \nabla\rho(\vec{r},t) \tag{13.16}$$

where D is known as the diffusion coefficient of the system. The equation of continuity is

$$\frac{\partial}{\partial t}\rho(\vec{r},t) + \nabla.\ \vec{J}(\vec{r},t) = 0 \tag{13.17}$$

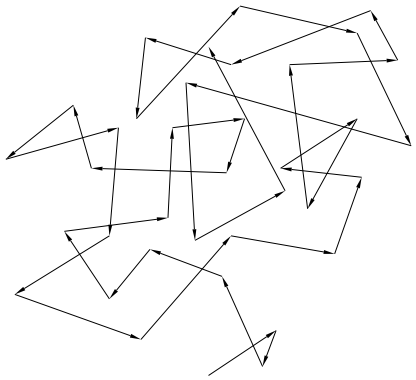


Figure 2: A part of the Brownian motion of a fine particle suspended in a fluid.

Using equation (13.16) in (13.17) we have

$$\frac{\partial}{\partial t}\rho(\vec{r},t) = D\ \nabla^2\rho(\vec{r},t) \tag{13.18}$$

Solution of equation (13.18) is[4]

$$\rho(\vec{r},t) = \frac{N}{8(\pi Dt)^{3/2}}\ \exp\Big(-\frac{r^2}{4Dt}\Big) \tag{13.19}$$

[4]It can be verified by substituting this solution in the equation. Let

$$\rho(\vec{r},t) = \frac{N}{(4\pi Dt)^{3/2}}\exp\Big(-\frac{r^2}{4Dt}\Big) = A\ \exp\Big(-\frac{r^2}{4Dt}\Big)$$

Therefore,

$$\nabla^2\rho = \frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\ \frac{\partial\rho}{\partial r}\Big) = -\frac{A}{2Dtr^2}\ \frac{\partial}{\partial r}\Big[r^3\ \exp\Big(-\frac{r^2}{4Dt}\Big)\Big]$$

where N is the total number of particles in the fluid. Equation (13.19) is normalized so that[5]

$$\int_0^\infty \rho(\vec{r}, t)\ 4\pi r^2\ \mathrm{d}r = N$$

Equation (13.19) can be used to calculate ensemble average of physical quantities. The average of r^2 is

$$\langle r^2 \rangle = \frac{1}{N} \int_0^\infty r^2\ \rho(\vec{r}, t) 4\pi r^2 \mathrm{d}r = \frac{4\pi}{N} \int_0^\infty r^4 \rho(\vec{r}, t)\ \mathrm{d}r$$

$$= \frac{1}{2\sqrt{\pi}(Dt)^{3/2}} \int_0^\infty r^4 \exp\Big(- \frac{r^2}{4Dt}\Big)\ \mathrm{d}r \tag{13.20}$$

Let $r = 2\sqrt{Dt}\ u^{1/2}$ and thus $\mathrm{d}r = \sqrt{Dt}\ u^{-1/2}\mathrm{d}u$. Equation (13.20) gives

$$\langle r^2 \rangle = \frac{8Dt}{\sqrt{\pi}} \int_0^\infty \exp(-u)\ u^{3/2} \mathrm{d}u = \frac{8Dt}{\sqrt{\pi}}\ \Gamma(5/2) = 6Dt \tag{13.21}$$

For one-dimensional problem, we have

$$\rho(x, t) = \frac{N}{(4\pi Dt)^{1/2}}\ \exp\Big(- \frac{x^2}{4Dt}\Big)$$

$$= -\frac{A}{2Dtr^2}\Big[3r^2 \exp\Big(- \frac{r^2}{4Dt}\Big) - \frac{r^4}{2Dt} \exp\Big(- \frac{r^2}{4Dt}\Big)\Big]$$

and

$$D\ \nabla^2 \rho = -\frac{A}{2t}\ \exp\Big(- \frac{r^2}{4Dt}\Big)\Big[3 - \frac{r^2}{2Dt}\Big]$$

We have

$$\frac{\partial \rho}{\partial t} = \frac{N}{(4\pi Dt)^{3/2}}\ \exp\Big(- \frac{r^2}{4Dt}\Big)\Big[\frac{r^2}{4Dt^2}\Big] - \frac{3N}{2t(4\pi Dt)^{3/2}} \exp\Big(- \frac{r^2}{4Dt}\Big)$$

$$= -\frac{A}{2t}\ \exp\Big(- \frac{r^2}{4Dt}\Big)\Big[3 - \frac{r^2}{2Dt}\Big]$$

Thus,

$$\frac{\partial \rho}{\partial t} = D\ \nabla^2 \rho$$

[5]Consider

$$I = \int_0^\infty \rho(\vec{r}, t) 4\pi r^2 \mathrm{d}r = \frac{N}{2\sqrt{\pi}(Dt)^{3/2}} \int_0^\infty r^2 \exp\Big(- \frac{r^2}{4Dt}\Big)\ \mathrm{d}r$$

Let $r = 2\sqrt{Dt}\ u^{1/2}$ and thus $\mathrm{d}r = \sqrt{Dt}\ u^{-1/2}\mathrm{d}u$. Then we have

$$I = \frac{2N}{\sqrt{\pi}} \int_0^\infty u^{1/2}\ \exp(-u)\ \mathrm{d}u = \frac{2N}{\sqrt{\pi}}\ \Gamma(3/2) = N$$

with normalization condition [6]

$$\int_{-\infty}^{\infty} \rho(x,t)\ \mathrm{d}x = N$$

The average of x^2 is

$$\langle x^2 \rangle = \frac{1}{N}\int_{-\infty}^{\infty} x^2\ \rho(x,t)\ \mathrm{d}x = \int_{-\infty}^{\infty} x^2 \frac{1}{(4\pi Dt)^{1/2}}\ \exp\Big(-\frac{x^2}{4Dt}\Big)\ \mathrm{d}x$$

$$= \frac{1}{(\pi Dt)^{1/2}}\int_0^{\infty} x^2\ \exp\Big(-\frac{x^2}{4Dt}\Big)\ \mathrm{d}x$$

Let $x = 2\sqrt{Dt}\ u^{1/2}$ and thus $\mathrm{d}x = \sqrt{Dt}\ u^{-1/2}\mathrm{d}u$. Thus, we have

$$\langle x^2 \rangle = \frac{4Dt}{\sqrt{\pi}}\int_0^{\infty} u^{1/2}\exp(-u)\ \mathrm{d}u = \frac{4Dt}{\sqrt{\pi}}\ \Gamma(3/2) = 2Dt \qquad (13.22)$$

Equations (13.21) and (13.22) show that the values of $\langle r^2 \rangle$ and $\langle x^2 \rangle$ increase with time t and therefore, the Brownian particles are concentrated initially at the origin (at time $t = 0$) and they diffuse out as the time passes. This diffusion process is irreversible as $\langle r^2 \rangle$ as well as $\langle x^2 \rangle$ go on increasing with time t. The irreversible behaviour of the phenomenon arises due to the random fluctuating forces exerted by the other molecules of the fluid.

3. Langevin theory

Langevin developed a simple theory for the motion of Brownian particles. He considered that the Brownian motion of a particle is a consequence of molecular collisions which exert random unbalanced force on the particle. Suppose $\vec{X}(t)$ be the force acting on the particle of mass m moving with velocity $\vec{v}$, then the equation of motion is

$$m\ \frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = \vec{X}(t) \qquad (13.23)$$

[6]The normalization condition is

$$I = \int_{-\infty}^{\infty} \rho(x,t)\ \mathrm{d}x = \int_0^{\infty} \frac{N}{(\pi Dt)^{1/2}}\ \exp\Big(-\frac{x^2}{4Dt}\Big)\ \mathrm{d}x$$

Let $x = 2\sqrt{Dt}\ u^{1/2}$ and thus $\mathrm{d}x = \sqrt{Dt}\ u^{-1/2}\ \mathrm{d}u$. Thus, we have

$$I = \frac{N}{\sqrt{\pi}}\int_0^{\infty} \exp(-u)\ u^{-1/2}\mathrm{d}u = \frac{N}{\sqrt{\pi}}\ \Gamma(1/2) = N$$

Here, the mean value of the fluctuating force may or may not be zero. In order to investigate the problem, Langevin made an important assumption by dividing the force $\vec{X}(t)$ into two components

$$\vec{X}(t) = -\beta m\vec{v} + \vec{F}(t) \tag{13.24}$$

where the first component $-\beta m\vec{v}$ represents the viscous drag on the particle and second component $\vec{F}(t)$ is the rapidly fluctuating force due to molecular collisions. Over a long interval of time, average of the force $\vec{F}(t)$ must obviously be zero, *i.e.,* $\langle\ \vec{F}(t)\rangle = 0$. Using equation (13.24) in (13.23), we have

$$m\ \frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = -\beta m\vec{v} + \vec{F}(t) \tag{13.25}$$

On taking time average of equation (13.25), we have

$$m\ \frac{\mathrm{d}\langle\vec{v}\ \rangle}{\mathrm{d}t} = -\beta m\langle\vec{v}\ \rangle + \langle\vec{F}(t)\rangle \qquad \text{or} \qquad m\ \frac{\mathrm{d}\langle\vec{v}\ \rangle}{\mathrm{d}t} = -\beta m\langle\vec{v}\ \rangle \tag{13.26}$$

Following Stokes law the viscous force acting on a spherical particle of radius a moving with velocity v in a medium of viscosity η is $6\pi a\eta v$ and the direction of the force is opposite to that of the motion of the particle. It gives

$$\beta mv = v6\pi a\eta v \qquad\qquad \text{or} \qquad\qquad \beta = \frac{6\pi a\eta}{m}$$

Equation (13.26) can be expressed as

$$\frac{\mathrm{d}\langle\vec{v}\ \rangle}{\langle\vec{v}\ \rangle} = -\frac{\mathrm{d}t}{\tau} \qquad \text{so that} \qquad \langle\vec{v}(t)\rangle = \vec{v}(0)\ \exp\Big(-\frac{t}{\tau}\Big)$$

where $\tau = 1/\beta$ is the relaxation time. This relation shows that average velocity of the particle decays to zero exponentially. Dividing equation (13.25) by m, we have

$$\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = -\beta\ \vec{v} + \vec{A}\ (t) \tag{13.27}$$

where $\vec{A}\ (t)\Big[\ \equiv\vec{F}\ (t)/m\Big]$ is the acceleration. For convenience, let us consider one-dimensional motion and multiply equation (13.27) by x to get

$$x\ \ddot{x} = -\beta x\ \dot{x} + xA(t) \tag{13.28}$$

Now,

$$\frac{\mathrm{d}}{\mathrm{d}t}(x^2) = 2x\ \dot{x} \qquad \text{and} \qquad \frac{\mathrm{d}^2}{\mathrm{d}t^2}(x^2) = 2x\ \ddot{x} + 2(\dot{x})^2$$

Thus,

$$x\ \ddot{x} = \frac{1}{2}\ \frac{\mathrm{d}^2}{\mathrm{d}t^2}(x^2) - (\dot{x})^2$$

Using these relations in equation (13.28) we have

$$\frac{1}{2}\ \frac{\mathrm{d}^2}{\mathrm{d}t^2}(x^2) - (\dot{x})^2 = -\frac{1}{2}\ \beta\ \frac{\mathrm{d}}{\mathrm{d}t}(x^2) + xA(t)$$

On taking time average of this equation and assuming that $\langle x\ A(t)\rangle = 0$, because average of the random force is zero, we have

$$\frac{1}{2}\ \frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle x^2\rangle + \frac{1}{2}\ \beta\ \frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle = \langle(\dot{x})^2\rangle \tag{13.29}$$

Brownian particles remain in thermal equilibrium and thus, the mean kinetic energy of each particle is

$$\frac{1}{2}\ m\langle(\dot{x})^2\rangle = \frac{1}{2}\ kT \qquad \text{or} \qquad \langle(\dot{x})^2\rangle = \frac{kT}{m} \tag{13.30}$$

where T is the equilibrium temperature. Using equation (13.30) in (13.29), we get

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle x^2\rangle + \beta\ \frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle = \frac{2kT}{m} \tag{13.31}$$

Let $u = (\mathrm{d}\langle x^2\rangle/\mathrm{d}t)$, then equation (13.31) can be written as

$$\frac{\mathrm{d}u}{\mathrm{d}t} + \beta u = \frac{2kT}{m} \qquad \text{or} \qquad \frac{\mathrm{d}u}{\mathrm{d}t} = -\beta\Big(u - \frac{2kT}{m\beta}\Big) \tag{13.32}$$

Let

$$w = u - \frac{2kT}{m\beta} \qquad \text{so that} \qquad \frac{\mathrm{d}w}{\mathrm{d}t} = \frac{\mathrm{d}u}{\mathrm{d}t} \tag{13.33}$$

then equation (13.32) becomes

$$\frac{\mathrm{d}w}{\mathrm{d}t} = -\beta\ w \qquad \text{or} \qquad \frac{\mathrm{d}w}{w} = -\beta \mathrm{d}t$$

Solution of this equation is

$$\ln\ w = -\beta t + \ln\ C \qquad \text{or} \qquad w = C\ \exp(-\beta t)$$

Substituting the expression for w in equation (13.33), we have

$$u = \frac{2kT}{m\beta} + C\,\exp(-\beta t)$$

Using the expression for u here, we get

$$\frac{\mathrm{d}\langle x^2\rangle}{\mathrm{d}t} = \frac{2kT}{m\beta} + C\,\exp(-\beta t) \tag{13.34}$$

The condition that at $t = 0$ we have $(\mathrm{d}/\mathrm{d}t)\langle x^2\rangle = 0$ gives the value of the constant C

$$C = -\frac{2kT}{m\beta}$$

Using the value of C, equation (13.34) can be written as

$$\frac{\mathrm{d}\langle x^2\rangle}{\mathrm{d}t} = \frac{2kT}{m\beta} - \frac{2kT}{m\beta}\,\exp(-\beta t) = \frac{2kT\tau}{m}\Big[1 - \exp(-t/\tau)\Big] \tag{13.35}$$

where $\tau = 1/\beta$. Integration of equation (13.35) gives

$$\langle x^2\rangle = \frac{2kT\tau}{m}\Big[t + \tau\,\exp(-t/\tau)\Big] + C' \tag{13.36}$$

The condition that at $t = 0$ we have $\langle x^2\rangle = 0$ and we can get the value of the constant C'

$$C' = -\frac{2kT\tau^2}{m}$$

Using the value of C', equation (13.36) can be written as

$$\langle x^2\rangle = \frac{2kT\tau^2}{m}\Big[\frac{t}{\tau} - \Big\{1 - \exp(-t/\tau)\Big\}\Big] \tag{13.37}$$

The transient state is given by the exponential term.

(i) When $t << \tau$, the exponential term can be expanded and equation (13.37) gives

$$\langle x^2\rangle = \frac{2kT\tau^2}{m}\Big[\frac{t}{\tau} - \Big\{1 - \Big(1 - \frac{t}{\tau} + \frac{1}{2}\frac{t^2}{\tau^2} - \ldots\Big)\Big\}\Big] \approx \frac{kT}{m}\,t^2 = \langle v^2\rangle\,t^2$$

This shows that the particles move with the thermal velocity $(kT/m)^{1/2}$ and

$$\langle x^2\rangle \propto t^2 \tag{13.38}$$

(ii) When $t >> \tau$, we can neglect $\exp(-t/\tau)$ and 1 in comparison to t/τ and equation (13.37) gives

$$\langle x^2 \rangle = \frac{2kT\tau^2}{m} \frac{t}{\tau} = \frac{2kT}{m\beta} t \tag{13.39}$$

This shows that the particles move with $\sqrt{2}$ times the thermal velocity $(kT/m)^{1/2}$ and

$$\langle x^2 \rangle \propto t \tag{13.40}$$

This relation is for a random walk and was first derived by Einstein. From equations (13.22) and (13.39), we have

$$2Dt = \frac{2kT}{m\beta} t \qquad \text{or} \qquad D = \frac{kT}{m\beta} = BkT \tag{13.41}$$

where B is the mobility of the system. Obviously, the diffusion coefficient D increase with the increase of T. This equation (13.41) is known as the Einstein equation. The relations (13.38) and (13.40) show the dependence on time.

4. Power spectrum of fluctuations

We already know that a physical quantity $A(t)$ varying with time t fluctuates about its mean value $\langle A \rangle$. Here, we shall discuss about a technique used for analyzing the time scale of the fluctuations. Let us consider a fluctuating quantity $A(t)$ for a long interval $0 < t < T$. For applying Fourier series analysis, such fluctuating quantities can be expressed as

$$A(t) = a_0 + \sum_{n=1}^{\infty} a_n \cos \omega_n t + \sum_{n=1}^{\infty} b_n \sin \omega_n t$$

where $\omega_n = 2\pi n/T$ with integer n and

$$a_0 = \frac{1}{T} \int_0^T A(t)\ \mathrm{d}t \qquad a_n = \frac{2}{T} \int_0^T A(t) \cos \omega_n t\ \mathrm{d}t$$

$$b_n = \frac{2}{T} \int_0^T A(t) \sin \omega_n t\ \mathrm{d}t$$

We assume that the mean square value $\langle [A(t)]^2 \rangle$ has approached to an equilibrium value, *i.e.*, $\langle [A(t)]^2 \rangle$ = constant. Such a quantity is said to be statistically stationary. When a physical quantity varies more or less

randomly with time, the Fourier coefficients are statistical in nature. The time average of $[A(t)]^2$ is

$$\overline{[A(t)]^2} = \frac{1}{T}\int_0^T \Big(a_0 + \sum_{n=1}^{\infty} a_n \cos\omega_n t + \sum_{n=1}^{\infty} b_n \sin\omega_n t\Big)^2 \, \mathrm{d}t$$

$$= \frac{1}{T}\int_0^T \Big(a_0^2 + \sum_{n=1}^{\infty}\sum_{k=1}^{\infty} a_n a_k \cos\omega_n t \;\cos\omega_k t$$

$$+ \sum_{n=1}^{\infty}\sum_{k=1}^{\infty} b_n b_k \sin\omega_n t \;\sin\omega_k t + 2a_0 \sum_{n=1}^{\infty} a_n \cos\omega_n t$$

$$+ 2a_0 \sum_{n=1}^{\infty} a_n \sin\omega_n t + 2\sum_{n=1}^{\infty}\sum_{k=1}^{\infty} a_n b_k \cos\omega_n t \;\sin\omega_k t\Big) \, \mathrm{d}t$$

Using the orthogonality properties of sine and cosine functions:

$$\int_0^T \sin\omega_i t \;\sin\omega_j t \; \mathrm{d}t = \begin{cases} (T/2)\;\delta_{ij} & \text{for } \omega_i \neq 0 \\ 0 & \text{for } \omega_i = 0 \end{cases} \tag{13.42}$$

$$\int_0^T \cos\omega_i t \;\cos\omega_j t \; \mathrm{d}t = \begin{cases} (T/2)\;\delta_{ij} & \text{for } \omega_i \neq 0 \\ T\;\delta_{ij} & \text{for } \omega_i = 0 \end{cases} \tag{13.43}$$

$$\int_0^T \sin\omega_i t \;\cos\omega_j t \; \mathrm{d}t = 0 \qquad \text{for all } \omega_i \text{ and } \omega_j \tag{13.44}$$

we get

$$\overline{[A(t)]^2} = a_0^2 + \frac{1}{2}\sum_{n=1}^{\infty} a_n^2 + \frac{1}{2}\sum_{n=1}^{\infty} b_n^2$$

The amount of power contained in a frequency $\nu \equiv \omega_n/2\pi = n/T$ is

$$\overline{[A(t)]^2} = \langle a_0^2\rangle + \frac{1}{2}\sum_{n=1}^{\infty}\langle a_n^2\rangle + \frac{1}{2}\sum_{n=1}^{\infty}\langle b_n^2\rangle$$

Due to randomness of the phases of various components, we have

$$\langle a_n^2\rangle = \langle b_n^2\rangle \qquad \text{for all } n$$

and thus,

$$\overline{[A(t)]}^2 = \sum_{n=0}^{\infty}\langle a_n^2\rangle$$

For large T, the separation between two frequencies may be taken very small. Let $\Delta\nu_n$ be a frequency bandwidth, which is the separation between two adjacent frequencies:

$$\Delta\nu_n = \nu_{n+1} - \nu_n = \frac{n+1}{T} - \frac{n}{T} = \frac{1}{T}$$

then we have

$$\langle A^2 \rangle = \sum_{n=0}^{\infty} G(\nu_n)\ \Delta\nu_n \approx \int_0^{\infty} G(\nu)\ \mathrm{d}\nu \tag{13.45}$$

where

$$\langle a_n^2 \rangle = G(\nu_n)\ \Delta\nu_n \tag{13.46}$$

The $G(\nu_n)$ is known as the spectral density of the randomly fluctuating quantity $A(t)$. Equation (13.45) represents the power spectrum of $A(t)$. We can now calculate the auto-correlation function $C_A(\tau)$ in terms of $G(\nu_n)$. Let us consider the correlation function

$$C_A(\tau) = \overline{A(t)\ A(t+\tau)}$$

where the average is taken over the time t. We can take an ensemble average of the time average

$$\begin{aligned} C_A(\tau) =& \langle \overline{A(t)\ A(t+\tau)} \rangle \\ &= \Big\langle \frac{1}{T} \int_0^T \Big(a_0 + \sum_{n=1}^{\infty} a_n \cos\omega_n t + \sum_{n=1}^{\infty} b_n \sin\omega_n t \Big) \\ &\times \Big(a_0 + \sum_{m=1}^{\infty} a_m \cos\omega_m (t+\tau) + \sum_{m=1}^{\infty} b_m \sin\omega_m (t+\tau) \Big)\ \mathrm{d}t \Big\rangle \end{aligned} \tag{13.47}$$

Using the expansions

$$\sin\omega_m(t+\tau) = \sin\omega_m t\ \cos\omega_m\tau + \cos\omega_m t\ \sin\omega_m\tau$$

and

$$\cos\omega_m(t+\tau) = \cos\omega_m t\ \cos\omega_m\tau - \sin\omega_m t\ \sin\omega_m\tau$$

in equation (13.47), we get

$$C_A(\tau) = \Big\langle \frac{1}{T} \int_0^T \Big(a_0 + \sum_{n=1}^{\infty} a_n \cos\omega_n t + \sum_{n=1}^{\infty} b_n \sin\omega_n t \Big)$$

$$\times\Big(a_0+\sum_{m=1}^{\infty}a_m[\cos\omega_m t\ \cos\omega_m\tau-\sin\omega_m t\ \sin\omega_m\tau]$$

$$+\sum_{m=1}^{\infty}b_m[\sin\omega_m t\ \cos\omega_m\tau+\cos\omega_m t\ \sin\omega_m\tau]\Big)\ \mathrm{d}t\Big\rangle$$

Using equations (13.42), (13.43) and (13.44) in this equation, we get

$$C_A(\tau)=\Big\langle a_0^2+\frac{1}{2}\sum_{n=1}^{\infty}a_n^2\cos\omega_m\tau+\frac{1}{2}\sum_{n=1}^{\infty}a_nb_n\sin\omega_n\tau$$

$$-\frac{1}{2}\sum_{n=1}^{\infty}a_nb_n\sin\omega_n\tau+\frac{1}{2}\sum_{n=1}^{\infty}b_n^2\cos\omega_m\tau\Big\rangle$$

$$=\Big\langle a_0^2\Big\rangle+\frac{1}{2}\sum_{n=1}^{\infty}\Big(\Big\langle a_n^2\Big\rangle+\Big\langle b_n^2\Big\rangle\Big)\cos\omega_m\tau$$

Due to randomness of the phases of various components, we have

$$\langle a_n^2\rangle=\langle b_n^2\rangle\qquad\text{for all}\ \ n$$

we have

$$C_A(\tau)=\sum_{n=0}^{\infty}\langle a_n^2\rangle\cos\omega_n\tau \tag{13.48}$$

Using equation (13.46) in (13.48), we get

$$C_A(\tau)=\sum_{n=0}^{\infty}G(\nu_n)\ \Delta\nu_n\cos\omega_n t\approx\int_0^{\infty}G(\nu)\cos(2\pi\nu\tau)\ \mathrm{d}\nu \tag{13.49}$$

For $\tau=0$, equation (13.49) gives an important result

$$C_A(0)=\int_0^{\infty}G(\nu)\ \mathrm{d}\nu=\langle A^2\rangle$$

Equation (13.49) establishes a relation between the correlation function $C_A(\tau)$ and the power spectrum $G(\nu)$ and obviously shows that $C_A(\tau)$ is the Fourier cosine transform of $G(\nu)$. Hence, the inverse relation is

$$G(\nu)=\frac{2}{\pi}\int_0^{\infty}C_A(\tau)\cos(2\pi\nu\ \tau)\ \mathrm{d}(2\pi\tau)$$

$$=4\int_0^{\infty}C_A(\tau)\cos(2\pi\nu\tau)\ \mathrm{d}\tau \tag{13.50}$$

Equation (13.50) along with (13.49) is known as the Wiener-Khintchine theorem, which tells how rapidly the random process is changing. Let us consider that the fluctuations decay exponentially with time as

$$C_A(\tau) = C_A(0)\ \exp(-\tau/\tau_c) \tag{13.51}$$

where τ_c is known as the relaxation time. Variation of $C_A(\tau)/C_A(0)$ versus τ/τ_c is shown in Figure 3. Using equation (13.51) in (13.50), we get

$$G(\nu) = 4\int_0^\infty C_A(0)\ \exp(-\tau/\tau_c)\cos(2\pi\nu\tau)\ \mathrm{d}\tau$$

$$= 4C_A(0)\int_0^\infty \exp(-\tau/\tau_c)\cos(2\pi\nu\tau)\ \mathrm{d}\tau$$

$$= 4C_A(0)\Big[\frac{\exp(-\tau/\tau_c)}{(2\pi\nu)^2 + (1/\tau_c)^2}\Big\{ -\frac{1}{\tau_c}\cos(2\pi\nu\tau) + (2\pi\nu\tau)\sin(2\pi\nu\tau)\Big\}\Big]_0^\infty$$

$$= \frac{G(0)}{1 + (2\pi\nu\tau_c)^2}$$

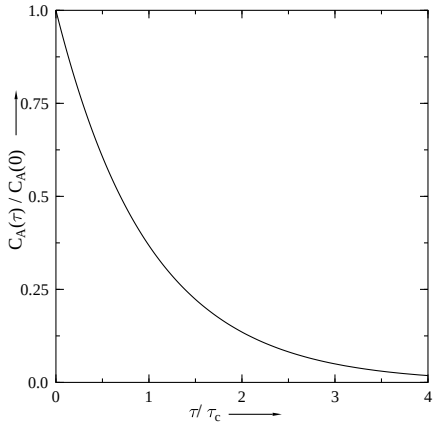


Figure 3: Variation of $C_A(\tau)/C_A(0)$ versus τ/τ_c.

where $G(0) = 4C_A(0)\tau_c$. Variation of $G(\nu)/G(0)$ versus $\log(2\pi\nu)$ for $\tau_c = 10^{-4}$ is shown in Figure 4. The power spectrum is flat for frequencies less than $1/2\pi\tau_c$, but decreases rapidly to zero at high frequencies.

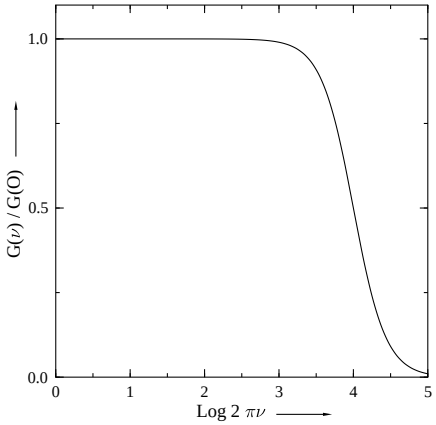


Figure 4: Variation of $G(\nu)/G(0)$ versus $\log(2\pi\nu)$ for $\tau_c = 10^{-4}$.

5. Fluctuation-dissipation theorem

A large number of macroscopic particles moving in a fluid are being bombarded continuously by the fluid particles which ultimately bring the motion to stop. Following the conservation law of energy, the kinetic energy of the particles is thereby converted into the heat and thus is dissipated. The microscopic interactions are associated with the fluctuations in the motions of the particles. Thus, the fluctuations affect the motion of the bodies through the process of energy dissipation. We shall discuss a relationship between the fluctuations and energy dissipation. This relation is known as the fluctuation-dissipation theorem.

Let us consider the Langevin equation for one-dimensional Brownian motion

$$\frac{\mathrm{d}v(t')}{\mathrm{d}t'} = -\beta v(t') + A(t')$$

Multiplying both sides by $\exp(\beta t')$ and rearranging we get

$$\mathrm{e}^{\beta t'}\ \frac{\mathrm{d}v(t')}{\mathrm{d}t'} + \beta\ \mathrm{e}^{\beta t'}\ v(t') = A(t')\ \mathrm{e}^{\beta t'}$$

$$\frac{\mathrm{d}}{\mathrm{d}t'}\Big(v\ \mathrm{e}^{\beta t'}\Big) = A(t')\ \ \mathrm{e}^{\beta t'}$$

On integrating this equation between the limits from $t' = 0$ to $t' = t$, we get

$$\Big[v\ \mathrm{e}^{\beta t'}\Big]_0^t = \int_0^t A(t')\ \mathrm{e}^{\beta t'}\mathrm{d}t'$$

$$v(t)\ \mathrm{e}^{\beta t} - v(0) = \int_0^t A(t')\ \mathrm{e}^{\beta t'} \mathrm{d}t'$$

$$v(t) = v(0)\ \mathrm{e}^{-\beta t} + \mathrm{e}^{-\beta\ t} \int_0^t A(t')\ \mathrm{e}^{\beta t'} \mathrm{d}t' \tag{13.52}$$

Since $\langle A(t') \rangle = 0$, from this equation, the average drift velocity is

$$\langle v(t) \rangle = v(0)\ \mathrm{e}^{-\beta t} + \mathrm{e}^{-\beta t} \int_0^t \langle A(t') \rangle\ \mathrm{e}^{\beta t'} \mathrm{d}t'$$

$$= v(0)\ \mathrm{e}^{-\beta t} + \mathrm{e}^{-\beta t} \langle A(t') \rangle \int_0^t \mathrm{e}^{\beta t'} \mathrm{d}t' = v(0)\ \mathrm{e}^{-\beta t}$$

It shows that the drift velocity of a particle decays exponentially to zero. Let us use equation (13.52) to calculate the mean square velocity $\langle v^2(t) \rangle$ as

$$\langle v^2(t) \rangle = \left\langle \left(v(0)\ \mathrm{e}^{-\beta t} + \mathrm{e}^{-\beta t} \int_0^t A(t') \mathrm{e}^{\beta t'} \mathrm{d}t' \right)^2 \right\rangle$$

$$= \left\langle v^2(0)\ \mathrm{e}^{-2\beta t} + \mathrm{e}^{-2\beta t} \int_0^t \int_0^t A(t') \mathrm{e}^{\beta t'} A(t'') \mathrm{e}^{\beta t''}\ \mathrm{d}t'\ \mathrm{d}t'' \right.$$

$$\left. + 2v(0)\ \mathrm{e}^{-2\beta t} \int_0^t A(t') \mathrm{e}^{\beta t'} \mathrm{d}t' \right\rangle$$

$$= v^2(0)\ \mathrm{e}^{-2\beta t} + \mathrm{e}^{-2\beta t} \int_0^t \int_0^t \mathrm{e}^{\beta(t'+t'')} \langle A(t') A(t'') \rangle\ \mathrm{d}t'\ \mathrm{d}t''$$

$$+ 2v(0)\ \mathrm{e}^{-2\beta t} \int_0^t \langle A(t') \rangle \mathrm{e}^{\beta t'} \mathrm{d}t'$$

$$= v^2(0)\ \mathrm{e}^{-2\beta t} + \mathrm{e}^{-2\beta t} \int_0^t \int_0^t\ \mathrm{e}^{\beta(t'+t'')} C_A(t', t'')\ \mathrm{d}t'\ \mathrm{d}t'' \tag{13.53}$$

where we used $\langle A(t') \rangle = 0$ and expressed

$$C_A(t', t'') = \langle A(t') A(t'') \rangle = \langle A(t') A(t' + s) \rangle = C_A(s)$$

It is the time auto-correlation function of the variable A. We have taken the time interval $s = t'' - t'$. This function provides the statistical correlation between the values of the fluctuating quantity A at the times t' and t''.

The fluctuation-dissipation theorem is a statement about the double time integral of $C_A(s)$. In order to evaluate double integral over $C_A(s)$ in equation (13.53), we introduce a new variable $u = (t' + t'')/2$, so that $\mathrm{d}t'\ \mathrm{d}t'' = \mathrm{d}s\ \mathrm{d}u$ and the double integral is[7]

$$I = \int_0^t \int_0^t \mathrm{e}^{\beta(t'+t'')} C_A(s)\ \mathrm{d}t'\ \mathrm{d}t'' = \int_{s=-\infty}^{\infty} \int_0^t \mathrm{e}^{2\beta u}\ C_A(s)\ \mathrm{d}s\ \mathrm{d}u$$

$$= \int_{s=-\infty}^{\infty} C_A(s)\ \mathrm{d}s \Big[\int_0^t \mathrm{e}^{2\beta u}\ \mathrm{d}u \Big] = \frac{1}{2\beta}[\exp(2\beta t) - 1]\ J \qquad (13.54)$$

where

$$J = \int_{-\infty}^{\infty} C_A(s)\ \mathrm{d}s = \int_{-\infty}^{\infty} \langle A(0)A(s)\rangle\ \ \mathrm{d}s = \frac{1}{m^2} \int_{-\infty}^{\infty} \langle F(0)F(s)\rangle\ \mathrm{d}s \quad (13.55)$$

Using equation (13.54) in (13.53), we have

$$\langle v^2(t)\rangle = v^2(0)\ \mathrm{e}^{-2\beta t} + \mathrm{e}^{-2\beta t}\ \frac{J}{2\beta}\Big[\exp(2\beta t) - 1\Big]$$

$$= v^2(0)\ \mathrm{e}^{-2\beta t} + \frac{J}{2\beta}\Big[1 - \exp(-2\beta t)\Big] \qquad (13.56)$$

When $t \to \infty$, the system attains the equilibrium state and we have (one-dimensional case)

$$\frac{1}{2}\ m\langle v^2\rangle = \frac{1}{2}\ kT$$

Using this relation in equation (13.56), we have

$$\frac{kT}{m} = 0 + \frac{J}{2\beta} \qquad \text{or} \qquad J = \frac{2kT\beta}{m} \qquad (13.57)$$

Comparison of equations (13.55) and (13.57) gives

$$\frac{2kT\beta}{m} = \frac{1}{m^2} \int_{-\infty}^{\infty} \langle F(0)F(s)\rangle\ \mathrm{d}s$$

or

$$\alpha \equiv \beta m = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle F(0)F(s)\rangle\ \mathrm{d}s = \frac{m^2}{2kT} \int_{-\infty}^{\infty} \langle A(0)A(s)\rangle\ \mathrm{d}s$$

This equation for the damping constant α is the fluctuation-dissipation theorem for Brownian particles. Equation (13.56) can be written as

$$\langle v^2(t)\rangle = v^2(0)\ \mathrm{e}^{-2\beta t} + \frac{kT}{m}\Big[1 - \exp(-2\beta t)\Big] + v^2(0) - v^2(0)$$

[7]When $t' = 0$ and $t'' = 0$, we have $u = 0$. When $t' = t$ and $t'' = t$, we have $u = t$.

$$= v^2(0) + \Big[\frac{kT}{m} - v^2(0)\Big]\Big[1 - \exp(-2\beta t)\Big]$$

When $v^2(0) = kT/m$, we have $v^2(t) = kT/m$. It shows that once the statistical equilibrium is attained, it has a natural tendency to persist. If the random force $F(t)$ producing fluctuations is large, the interaction between the macroscopic body and its medium is strong. It is possible that there exists relation between fluctuation and dissipation. If the system is not in equilibrium initially, then, in the presence of a strong interaction, the system will come rapidly in equilibrium. This situation is governed by the dissipation constant α. Hence, fluctuation-dissipation theorem establishes a relation between two opposing tendencies, characterized by $C_A(s)$ and α, which however have a common origin.

6. Fokker-Planck equation

Consider a system of particles moving in a fluid. For the probability function $f(v,t)$ that a particle has velocity v at time t, we shall derive here a differential equation, known as the Fokker-Planck equation. For convenience, let us consider one-dimensional velocity distribution. The technique is however applicable to any fluctuating quantity.

Let at any time t, $f(v,t)\mathrm{d}v$ denotes the probability that a particle in the system has a velocity between v and $v + \mathrm{d}v$. The distribution function $f(v,t)$ must satisfy the normalization condition

$$\int_{-\infty}^{\infty} f(v,t)\ \mathrm{d}v = 1$$

In the fluid, velocities of the particles go on changing regularly. Let $P(v,v')\ \mathrm{d}v$ denotes the probability that a particle having velocity v at time t, after a time interval τ has a velocity between v' and $v' + \mathrm{d}v'$. Here, $P(v,v')$ is known as the transition probability function. Then the velocity distribution at the time $t + \tau$ is

$$f(v', t+\tau) = \int_{-\infty}^{\infty} f(v,t)\ P(v,v')\ \mathrm{d}v \tag{13.58}$$

Let us introduce a new variable

$$\xi = v' - v \equiv v(t+\tau) - v(t)$$

so that $\mathrm{d}\xi = -\mathrm{d}v$ for the given v'. Then equation (13.58) becomes

$$f(v', t+\tau) = \int_{-\infty}^{\infty} f(v'-\xi, t) P(v'-\xi, \xi)\ \mathrm{d}\xi \tag{13.59}$$

Since we have only one velocity v', let us, for convenience, drop the prime (*i.e.,* replace v' by v) in equation (13.59) so that

$$f(v, t+\tau) = \int_{-\infty}^{\infty} f(v-\xi, t) P(v-\xi, \xi)\, \mathrm{d}\xi \tag{13.60}$$

Suppose in the small interval τ, the velocities of the particles change only by a small amount and therefore the transition probability function $P(v, v')$ has a sharp peak around $v \approx v'$ and it falls rapidly to zero elsewhere. We can thus have Taylor series expansions for $f(v-\xi, t)$ and $P(v-\xi, \xi)$ in the powers of ξ

$$f(v-\xi, t) = f(v, t) - \xi\, \frac{\partial}{\partial v} f(v, t) + \frac{\xi^2}{2} \frac{\partial^2}{\partial v^2} f(v, t) - \ldots \tag{13.61}$$

and

$$P(v-\xi, \xi) = P(v, \xi) - \xi\, \frac{\partial}{\partial v} P(v, \xi) + \frac{\xi^2}{2} \frac{\partial^2}{\partial v^2} P(v, \xi) - \ldots \tag{13.62}$$

We can also have Taylor series expansion of $f(v, t+\tau)$ in the powers of τ as

$$f(v, t+\tau) = f(v, t) + \tau\, \frac{\partial}{\partial t} f(v, t) + \ldots \tag{13.63}$$

Substituting equations (13.61), (13.62) and (13.63) in (13.60) and neglecting higher order terms, we have

$$f(v,t) + \tau\, \frac{\partial}{\partial t} f(v,t) = \int_{-\infty}^{\infty} \Big[f(v,t) - \xi\, \frac{\partial}{\partial v} f(v,t) + \frac{\xi^2}{2} \frac{\partial^2}{\partial v^2} f(v,t) \Big]$$

$$\Big[P(v,\xi) - \xi\, \frac{\partial}{\partial v} P(v,\xi) + \frac{\xi^2}{2} \frac{\partial^2}{\partial v^2} P(v,\xi) \Big]\, \mathrm{d}\xi$$

$$= \int_{-\infty}^{\infty} f(v,t) P(v,\xi)\, \mathrm{d}\xi - \int_{-\infty}^{\infty} f(v,t) \xi\, \frac{\partial P}{\partial v}\, \mathrm{d}\xi + \frac{1}{2} \int_{-\infty}^{\infty} f(v,t) \xi^2\, \frac{\partial^2 P}{\partial v^2}\, \mathrm{d}\xi$$

$$- \int_{-\infty}^{\infty} P(v,\xi) \xi\, \frac{\partial f}{\partial v}\, \mathrm{d}\xi + \int_{-\infty}^{\infty} \xi^2\, \frac{\partial f}{\partial v}\, \frac{\partial P}{\partial v}\, \mathrm{d}\xi + \int_{-\infty}^{\infty} P(v,\xi) \frac{\xi^2}{2} \frac{\partial^2 f}{\partial v^2}\, \mathrm{d}\xi$$

Thus,

$$f(v,t) + \tau\, \frac{\partial}{\partial t} f(v,t) = f(v,t) \int_{-\infty}^{\infty} P(v,\xi)\, \mathrm{d}\xi - f(v,t) \int_{-\infty}^{\infty} \xi\, \frac{\partial P}{\partial v}\, \mathrm{d}\xi$$

$$+ \frac{1}{2}\, f(v,t)\, \int_{-\infty}^{\infty} \xi^2\, \frac{\partial^2 P}{\partial v^2}\, \mathrm{d}\xi - \frac{\partial f}{\partial v} \int_{-\infty}^{\infty} \xi P(v,\xi)\, \mathrm{d}\xi$$

$$+\frac{\partial f}{\partial v}\int_{-\infty}^{\infty}\xi^2\ \frac{\partial P}{\partial v}\ \mathrm{d}\xi+\frac{1}{2}\ \frac{\partial^2 f}{\partial v^2}\int_{-\infty}^{\infty}P(v,\xi)\xi^2\ \mathrm{d}\xi \qquad (13.64)$$

Due to normalization condition

$$\int_{-\infty}^{\infty}P(v,\xi)\ \mathrm{d}\xi=1$$

we have

$$\gamma(v)=\frac{1}{\tau}\int_{-\infty}^{\infty}\xi P(v,\xi)\ \mathrm{d}\xi=\frac{\langle\xi\rangle}{\tau}$$

$$\frac{\partial\gamma}{\partial v}=\frac{1}{\tau}\int_{-\infty}^{\infty}\xi\ \frac{\partial P}{\partial v}\ \mathrm{d}\xi \qquad\qquad \frac{\partial^2\gamma}{\partial v^2}=\frac{1}{\tau}\int_{-\infty}^{\infty}\xi\ \frac{\partial^2 P}{\partial v^2}\ \mathrm{d}\xi$$

$$\delta(v)=\frac{1}{\tau}\int_{-\infty}^{\infty}\xi^2\ P(v,\xi)\ \mathrm{d}\xi=\frac{\langle\xi^2\rangle}{\tau}$$

$$\frac{\partial\delta}{\partial v}=\frac{1}{\tau}\int_{-\infty}^{\infty}\xi^2\ \frac{\partial P}{\partial v}\ \mathrm{d}\xi \qquad\qquad \frac{\partial^2\delta}{\partial v^2}=\frac{1}{\tau}\int_{-\infty}^{\infty}\xi^2\ \frac{\partial^2 P}{\partial v^2}\ \mathrm{d}\xi$$

Using these relations, equation (13.64) becomes

$$\frac{\partial}{\partial t}f(v,t)=-f\ \frac{\partial\gamma}{\partial v}+\frac{f}{2}\frac{\partial^2\delta}{\partial v^2}-\frac{\partial f}{\partial v}\ \gamma+\frac{\partial f}{\partial v}\ \frac{\partial\delta}{\partial v}+\frac{1}{2}\frac{\partial^2 f}{\partial v^2}\ \delta$$

$$=-\Big[f\ \frac{\partial\gamma}{\partial v}+\gamma\ \frac{\partial f}{\partial v}\Big]+\frac{1}{2}\Big[f\ \frac{\partial^2\delta}{\partial v^2}+2\frac{\partial f}{\partial v}\frac{\partial\delta}{\partial v}+\delta\ \frac{\partial^2 f}{\partial v^2}\Big]$$

$$=-\frac{\partial}{\partial v}(f\gamma)+\frac{1}{2}\frac{\partial^2}{\partial v^2}(f\delta) \qquad (13.65)$$

This equation is known as the Fokker-Planck equation which plays an important role in the theory of fluctuations and Brownian motion. It is applicable to a variety of random processes for calculation of probability density of a transition.

6.1 Diffusion equation

When the probability function $P(v, \xi)$ is symmetric for ξ, we have $\gamma = 0$ and if we assume that δ is independent of velocity v, the Fokker-Planck equation (13.65) reduces to

$$\frac{\partial f}{\partial t} = \frac{\delta}{2} \frac{\partial^2 f}{\partial v^2} \tag{13.66}$$

It is identical to the diffusion equation (Fick's law) with diffusion coefficient $D = \delta/2$.

Let us apply this equation to a system of particles with initial velocity v_0. Solution of equation (13.66) is[8]

$$f(v, t) = \frac{1}{2\sqrt{\pi D t}} \exp\Big(-\frac{(v - v_0)^2}{4Dt}\Big) \tag{13.67}$$

For this distribution function (13.67), let us calculate the mean square deviation of velocity of a particle from the initial velocity v_0 during the time interval τ as

$$\langle (v - v_0)^2 \rangle = \int_{-\infty}^{\infty} (v - v_0)^2 f(v, \tau)\ \mathrm{d}v$$

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[8] We have

$$\frac{\partial f}{\partial v} = \frac{1}{2\sqrt{\pi D t}} \exp\Big(-\frac{(v - v_0)^2}{4Dt}\Big)\Big[-\frac{(v - v_0)}{2Dt}\Big]$$

$$\frac{\partial^2 f}{\partial v^2} = \frac{1}{2\sqrt{\pi D t}} \exp\Big(-\frac{(v - v_0)^2}{4Dt}\Big)\Big[\frac{(v - v_0)^2}{4D^2 t^2}\Big] + \frac{1}{2\sqrt{\pi D t}} \exp\Big(-\frac{(v - v_0)^2}{4Dt}\Big)\Big[-\frac{1}{2Dt}\Big]$$

$$D\,\frac{\partial^2 f}{\partial v^2} = \frac{1}{2\sqrt{\pi D t}} \exp\Big(-\frac{(v - v_0)^2}{4Dt}\Big)\Big[\frac{(v - v_0)^2}{4Dt^2} - \frac{1}{2t}\Big]$$

Now,

$$\frac{\partial f}{\partial t} = -\frac{1}{4t\sqrt{\pi D t}} \exp\Big(-\frac{(v - v_0)^2}{4Dt}\Big) + \frac{1}{2\sqrt{\pi D t}} \exp\Big(-\frac{(v - v_0)^2}{4Dt}\Big)\Big[\frac{(v - v_0)^2}{4Dt^2}\Big]$$

$$= \frac{1}{2\sqrt{\pi D t}} \exp\Big(-\frac{(v - v_0)^2}{4Dt}\Big)\Big[\frac{(v - v_0)^2}{4Dt^2} - \frac{1}{2t}\Big]$$

Thus,

$$\frac{\partial f}{\partial t} = D\,\frac{\partial^2 f}{\partial v^2}$$

$$= \frac{1}{\sqrt{\pi D\tau}} \int_0^\infty (v - v_0)^2 \exp\Big(- \frac{(v - v_0)^2}{4D\tau}\Big)\ \mathrm{d}v$$

Let $(v - v_0) = 2\sqrt{D\tau}\ x^{1/2}$ so that $\mathrm{d}v = \sqrt{D\tau}\ x^{-1/2}\ \mathrm{d}x$. Then we have

$$\langle (v - v_0)^2 \rangle = \frac{4D\tau}{\sqrt{\pi}} \int_0^\infty x^{1/2} \exp(-x)\ \mathrm{d}x = \frac{4D\tau}{\sqrt{\pi}}\ \Gamma(3/2) = 2D\tau = \frac{2kT}{m\beta}\ \tau$$

where we have used the equation (13.41).

6.2 Brownian motion

The Fokker-Planck equation can be applied for the Brownian motion of particles in a gas. The Langevin equation for a Brownian particle is

$$\frac{\mathrm{d}v}{\mathrm{d}t} = -\beta v + A(t) \tag{13.68}$$

For a small interval τ, we have

$$\xi = v(t + \tau) - v(t) = \int_t^{t+\tau} [-\beta v + A(t')]\ \mathrm{d}t'$$

$$= -\beta v[t + \tau - t] + \int_t^{t+\tau} A(t')\ \mathrm{d}t' = -\beta v\tau + K(\tau) \tag{13.69}$$

where

$$K(\tau) = \int_t^{t+\tau} A(t')\ \mathrm{d}t'$$

As $A(t')$ is random variable of average zero, we have $\langle K(\tau) \rangle = 0$ and thus, $\langle \xi \rangle = -\beta v\tau$. Let us consider the Langevin equation for one-dimensional Brownian motion

$$\frac{\mathrm{d}v(t')}{\mathrm{d}t'} = -\beta v(t') + A(t')$$

Multiplying both sides by $\exp(\beta\ t')$ and rearranging we get

$$\mathrm{e}^{\beta t'}\ \frac{\mathrm{d}v(t')}{\mathrm{d}t'} + \beta\ \mathrm{e}^{\beta t'} v(t') = A(t')\ \mathrm{e}^{\beta t'}$$

$$\frac{\mathrm{d}}{\mathrm{d}t'}\Big(v\ \mathrm{e}^{\beta t'}\Big) = A(t')\ \mathrm{e}^{\beta t'}$$

On integrating this equation between the limits from $t' = t$ to $t' = t + \tau$, we get

$$\Big[v\ \mathrm{e}^{\beta t'}\Big]_t^{t+\tau} = \int_t^{t+\tau} A(t')\ \mathrm{e}^{\beta t'} \mathrm{d}t'$$

$$v(t+\tau)\ \mathrm{e}^{\beta(t+\tau)} - v(t)\ \mathrm{e}^{\beta t} = \int_t^{t+\tau} A(t')\ \mathrm{e}^{\beta t'}\mathrm{d}t'$$

$$\mathrm{e}^{\beta(t+\tau)}\Big[v(t+\tau) - v(t)\ \mathrm{e}^{-\beta\tau}\Big] = \int_t^{t+\tau} A(t')\ \mathrm{e}^{\beta t'}\mathrm{d}t' \qquad (13.70)$$

Let us use to calculate the mean square of equation (13.71) as

$$\mathrm{e}^{2\beta(t+\tau)}\Big\langle\Big[v(t+\tau) - v(t)\ \mathrm{e}^{-\beta\tau}\Big]^2\Big\rangle = \Big\langle \int_t^{t+\tau}\int_t^{t+\tau} A(t')\ \mathrm{e}^{\beta t'} A(t'')\mathrm{e}^{\beta t''}\mathrm{d}t'\mathrm{d}t''\Big\rangle$$

$$= \int_t^{t+\tau}\ \int_t^{t+\tau} \mathrm{e}^{\beta(t'+t'')} C_A(t',t'')\mathrm{d}t'\mathrm{d}t'' \qquad (13.71)$$

where we expressed

$$C_A(t',t'') = \langle A(t')A(t'')\rangle = \langle A(t')A(t'+s)\rangle = C_A(s)$$

is the time auto-correlation function of the variable A. We have taken the time interval $s = t''-t'$. This function provides the statistical correlation between the values of the fluctuating quantity A at the times t' and t''.

The fluctuation-dissipation theorem is a statement about the double time integral of $C_A(s)$. In order to evaluate double integral over $C_A(s)$ in equation (13.70), we introduce a new variable $u = (t'+t'')/2$, so that $\mathrm{d}t'\ \mathrm{d}t'' = \mathrm{d}s\ \mathrm{d}u$ and the double integral is[9]

$$I = \int_t^{t+\tau}\int_t^{t+\tau} \mathrm{e}^{\beta(t'+t'')} C_A(s)\mathrm{d}t'\mathrm{d}t'' = \int_{s=-\infty}^{\infty}\int_t^{t+\tau} \mathrm{e}^{2\beta u} C_A(s)\ \mathrm{d}s\mathrm{d}u$$

$$= \int_{s=-\infty}^{\infty} C_A(s)\ \mathrm{d}s\Big[\int_t^{t+\tau} \mathrm{e}^{2\beta u}\mathrm{d}u\Big] = \frac{J}{2\beta}[\mathrm{e}^{2\beta(t+\tau)} - \mathrm{e}^{2\beta t}]$$

$$= \frac{J}{2\beta}\mathrm{e}^{2\beta(t+\tau)}[1 - \mathrm{e}^{-2\beta\tau}] \qquad (13.72)$$

where

$$J = \int_{-\infty}^{\infty} C_A(s)\ \mathrm{d}s = \int_{-\infty}^{\infty}\langle A(0)A(s)\rangle\ \mathrm{d}s = \frac{1}{m^2}\int_{-\infty}^{\infty}\langle F(0)F(s)\rangle\ \mathrm{d}s \qquad (13.73)$$

Using equation (13.72) in (13.71), we have

$$\mathrm{e}^{2\beta(t+\tau)}\Big\langle\Big[v(t+\tau) - v(t)\ \mathrm{e}^{-\beta\tau}\Big]^2\Big\rangle = \frac{J}{2\beta}\mathrm{e}^{2\beta(t+\tau)}[1 - \mathrm{e}^{-2\beta\tau}]$$

[9]When $t' = 0$ and $t'' = 0$, we have $u = 0$. When $t' = t$ and $t'' = t$, we have $u = t$.

$$\left\langle \left[v(t+\tau) - v(t)\ \mathrm{e}^{-\beta\tau} \right]^2 \right\rangle = \frac{J}{2\beta}[1 - \mathrm{e}^{-2\beta\tau}]$$

$$\left\langle \left[\{v(t+\tau) - v(t)\} + v(t)\left(1 - \mathrm{e}^{-\beta\tau}\right) \right]^2 \right\rangle = \frac{kT}{m}\ [1 - \mathrm{e}^{-2\beta\tau}]$$

$$\left\langle \left[\xi + v(t)\left(1 - \mathrm{e}^{-\beta\tau}\right) \right]^2 \right\rangle = \frac{kT}{m}[1 - \mathrm{e}^{-2\beta\tau}]$$

$$\left\langle \xi^2 + v^2(t)\left(1 - \mathrm{e}^{-\beta\tau}\right)^2 + 2\xi v(t)\left(1 - \mathrm{e}^{-\beta\tau}\right) \right\rangle = \frac{kT}{m}[1 - \mathrm{e}^{-2\beta\tau}]$$

$$\langle \xi^2 \rangle + 2\langle \xi \rangle\ \langle v(t) \rangle \left(1 - \mathrm{e}^{-\beta\tau}\right) + \langle v^2(t) \rangle \left(1 - \mathrm{e}^{-\beta\tau}\right)^2 = \frac{kT}{m}[1 - \mathrm{e}^{-2\beta\tau}]$$

In the limit $\beta\tau << 1$, we have

$$\langle \xi^2 \rangle + 2\langle \xi \rangle \langle v(t) \rangle \beta\tau + \langle v^2(t) \rangle \beta^2\tau^2 = \frac{kT}{m}\ 2\beta\tau$$

$$\langle \xi^2 \rangle - 2\beta v\tau \langle v(t) \rangle \beta\tau + \langle v^2(t) \rangle \beta^2\tau^2 = \frac{kT}{m}\ 2\beta\tau$$

$$\langle \xi^2 \rangle = \frac{2kT\beta}{m}\ \tau + O(\tau^2)$$

For Brownian particles, we have

$$\gamma = \frac{\langle \xi \rangle}{\tau} = -\frac{\beta v\tau}{\tau} = -\beta v \qquad \text{and} \qquad \delta = \frac{\langle \xi^2 \rangle}{\tau} = \frac{2kT\beta}{m} = 2D_0$$

where

$$D_0 = \frac{kT\beta}{m} \tag{13.74}$$

The Fokker-Planck equation becomes

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial v}(f\gamma) + \frac{1}{2}\frac{\partial^2}{\partial v^2}(f\delta) = \frac{\partial}{\partial v}(f\beta v) + \frac{1}{2}\frac{\partial^2}{\partial v^2}(2fD_0)$$

$$= f\beta + \beta v\frac{\partial f}{\partial v} + D_0\ \frac{\partial^2 f}{\partial v^2} \tag{13.75}$$

Let us apply this equation to a system of Brownian particles with initial velocity v_0 at $t = 0$. For solving this equation, let us introduce a new variable

$$s = v\ \mathrm{e}^{\beta t} \tag{13.76}$$

Thus,

$$f(v,t) = f[s\ \mathrm{e}^{-\beta t}, t] = R(s,t)\ \mathrm{e}^{\beta t} \tag{13.77}$$

On differentiating equation (13.77), we get

$$\frac{\partial f}{\partial v} = \frac{\partial f}{\partial s}\ \frac{\partial s}{\partial v} = \mathrm{e}^{\beta t}\frac{\partial R}{\partial s}\ \mathrm{e}^{\beta t} = \mathrm{e}^{2\beta t}\frac{\partial R}{\partial s}$$

$$\frac{\partial^2 f}{\partial v^2} = \frac{\partial}{\partial s}\Big(\mathrm{e}^{2\beta t}\frac{\partial R}{\partial s}\Big)\ \frac{\partial s}{\partial v} = \mathrm{e}^{2\beta t}\frac{\partial^2 R}{\partial s^2}\ \mathrm{e}^{\beta t} = \mathrm{e}^{3\beta t}\ \frac{\partial^2 R}{\partial s^2}$$

and

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial t}\Big(R(s,t)\ \mathrm{e}^{\beta t}\Big) = \beta\ \mathrm{e}^{\beta t}R + \mathrm{e}^{\beta t}\frac{\partial R}{\partial t} + \mathrm{e}^{\beta t}\frac{\partial R}{\partial s}\frac{\partial s}{\partial t}$$

$$= \beta\ \mathrm{e}^{\beta t}R + \mathrm{e}^{\beta t}\frac{\partial R}{\partial t} + \mathrm{e}^{\beta t}\frac{\partial R}{\partial s}\beta v\ \mathrm{e}^{\beta t}$$

$$= \beta\ \mathrm{e}^{\beta t}R + \mathrm{e}^{\beta t}\frac{\partial R}{\partial t} + \beta v\ \mathrm{e}^{2\beta t}\frac{\partial R}{\partial s}$$

Using these expressions in equation (13.75), we get

$$\beta\ \mathrm{e}^{\beta t}R + \mathrm{e}^{\beta t}\frac{\partial R}{\partial t} + \beta v\ \mathrm{e}^{2\beta t}\frac{\partial R}{\partial s} = R\mathrm{e}^{\beta t}\beta + \beta v\ \mathrm{e}^{2\beta t}\ \frac{\partial R}{\partial s} + D_0\ \mathrm{e}^{3\beta t}\ \frac{\partial^2 R}{\partial s^2}$$

$$\mathrm{e}^{\beta t}\frac{\partial R}{\partial t} = D_0\ \mathrm{e}^{3\beta t}\frac{\partial^2 R}{\partial s^2} \qquad \text{or} \qquad \frac{\partial R}{\partial t} = D_0\ \mathrm{e}^{2\beta t}\frac{\partial^2 R}{\partial s^2} \tag{13.78}$$

It can be further simplified by introducing a new variable

$$z = \frac{1}{2\beta}[\mathrm{e}^{2\beta t} - 1] \tag{13.79}$$

so that

$$\frac{\partial R}{\partial t} = \frac{\partial R}{\partial z}\frac{\partial z}{\partial t} = \mathrm{e}^{2\beta t}\frac{\partial R}{\partial z}$$

Then equation (13.78) becomes

$$\frac{\partial R}{\partial z} = D_0\ \frac{\partial^2 R}{\partial s^2}$$

It is one-dimensional diffusion equation with the solution[10]

$$R = \frac{1}{\sqrt{4\pi D_0 z}} \exp\Big(-\frac{(s-v_0)^2}{4D_0 z}\Big) \tag{13.80}$$

where v_0 is a constant. Using equations (13.73), (13.75), (13.76), (13.77), (13.78 and (13.79), solution of equation (13.74) is

$$f = R\ \mathrm{e}^{\beta t} = \frac{1}{\sqrt{4\pi D_0 z}} \exp\Big(-\frac{(s-v_0)^2}{4D_0 z}\Big)\ \mathrm{e}^{\beta t}$$

$$= \Big(\frac{1}{4\pi(kT\beta/m)(1/2\beta)[\mathrm{e}^{2\beta t}-1]}\Big)^{1/2} \exp\Big(-\frac{(v\ \mathrm{e}^{\beta t}-v_0)^2}{4(kT\beta/m)(1/2\beta)[\mathrm{e}^{2\beta t}-1]}\Big)\mathrm{e}^{\beta t}$$

$$= \Big(\frac{m}{2\pi kT[1-\mathrm{e}^{-2\beta\ t}]}\Big)^{1/2} \exp\Big(-\frac{m(v-v_0\ \mathrm{e}^{-\beta t})^2}{2kT[1-\mathrm{e}^{-2\beta t}]}\Big) \tag{13.81}$$

For $\beta \to 0$, equation (13.81) reduces to

$$f(v,t) = \Big(\frac{m}{4\pi kT\beta\ t}\Big)^{1/2} \exp\Big(-\frac{m(v-v_0)^2}{4kT\beta t}\Big)$$

It is the case of pure diffusion. For $\beta\ t >> 0$, equation (13.81) reduces to

$$f = \Big(\frac{m}{2\pi kT}\Big)^{1/2} \exp\Big(-\frac{mv^2}{2kT}\Big)$$

It is the Maxwell distribution. Hence, with the elapse of time, the system of Brownian particles approaches a state of equilibrium under the influence of the restoring force and the particle collisions.

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[10] We have

$$\frac{\partial R}{\partial z} = \frac{1}{\sqrt{4\pi D_0 z}}\Big[\frac{(s-v_0)^2}{4\pi D_0 z^2}\Big]\exp\Big(-\frac{(s-v_0)^2}{4D_0 z}\Big) - \frac{1}{2z\ \sqrt{4\pi D_0 z}}\ \exp\Big(-\frac{(s-v_0)^2}{4D_0 z}\Big)$$

$$\frac{\partial R}{\partial s} = \frac{1}{\sqrt{4\pi D_0 z}}\ \Big[-\frac{(s-v_0)}{2D_0 z}\Big]\exp\Big(-\frac{(s-v_0)^2}{4D_0 z}\Big)$$

$$\frac{\partial^2 R}{\partial s^2} = \frac{1}{\sqrt{4\pi D_0 z}}\Big[\frac{(s-v_0)^2}{4D_0^2 z^2}\Big]\exp\Big(-\frac{(s-v_0)^2}{4D_0 z}\Big) - \frac{1}{2D_0 z\sqrt{4\pi D_0 z}}\exp\Big(-\frac{(s-v_0)^2}{4D_0 z}\Big)$$

$$D_0\frac{\partial^2 R}{\partial s^2} = \frac{1}{\sqrt{4\pi D_0 z}}\Big[\frac{(s-v_0)^2}{4D_0 z^2}\Big]\exp\Big(-\frac{(s-v_0)^2}{4D_0 z}\Big) - \frac{1}{2z\sqrt{4\pi D_0 z}}\exp\Big(x-\frac{(s-v_0)^2}{4D_0 z}\Big)$$

Thus,

$$\frac{\partial R}{\partial z} = D_0\frac{\partial^2 R}{\partial s^2}$$

7. Problems and questions

1. Discuss about the fluctuations in thermodynamics properties
2. Discuss about the fluctuations in entropy and in pressure.
3. Discuss about the fluctuations in volume and in temperature.
4. Show that the fluctuations of temperature and volume are statistically independent.
5. Show that the fluctuations of entropy and pressure are statistically independent.
6. What is Brownian motion? Discuss its theory.
7. Describe the Langevin theory for the motion of Brownian particles.
8. A Brownian particle satisfies the equation of motion

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle x^2\rangle + \frac{1}{\tau}\,\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle = \frac{2kT}{m}$$

   Show that

$$\langle x^2\rangle = \frac{2kT\tau^2}{m}\Big[\frac{t}{\tau} - \Big\{1 - \exp(-t/\tau)\Big\}\Big]$$

9. In the Brownian motion, the particles are initially centered at the origin. Show the particles diffuse in the outward direction as the time increases.
10. Show that the phenomenon of Brownian motion is irreversible.
11. Discuss about the power spectrum of fluctuations.
12. For the correlation function of the fluctuation given by

$$C_A(\tau) = C_A(0)\,\exp(-\tau/\tau_c)$$

    where τ_c is the relaxation time, show that the spectral density is

$$G(\nu) = \frac{4C_A(0)\tau_c}{1 + (2\pi\nu\tau_c)^2}$$

13. Describe the fluctuation-dissipation theorem.

14. Show that the mean square velocity of a Brownian particle starting at $t = 0$ is

$$\langle v^2(t)\rangle = v^2(0) + \Big[\frac{kT}{m} - v^2(0)\Big]\Big[1 - \exp(-2\beta t)\Big]$$

15. Derive Fokker-Planck function for fluctuations.

16. Apply Fokker-Planck equation for discussion of diffusion process.

17. Apply Fokker-Planck equation for discussion of Brownian motion of particles in a gas.

18. Write notes on the following

    (i) Brownian motion

    (ii) Langevin theory for Brownian particles

    (iii) Power spectrum of fluctuations

    (iv) Fluctuation-dissipation theorem

XIV. Numerical Simulation

Let us consider a system (gas) comprising N particles. The value of N is very large, as one gram mol of a gas contains 6.023×10^{23} molecules. This number is generally known as the Avogadro number. In a gas, the particles (molecules) move in a random manner under the influence of collisions with one another. Scientists envisaged that the trajectories of these particles can be calculated by writing the equations of motion (Newton's laws) and solving them. The process of doing so is known as the numerical simulation or numerical experiment. Before the invention of computers, such equations could not be solved for more than 3 particles. After the advent of computers, it is now possible to account for thousands of particles which involve millions of collisions. This simulation process where the Newton's laws of motion are involved is known as the numerical experiment of molecular motions. In such an experiment, positions and velocities of each molecule are calculated for a certain period of time with the help of a computer. Finally, each of the equilibrium quantities is obtained by averaging the respective parameters. For example, the kinetic temperature of a gas is calculated by averaging the kinetic energies of its constituent particles.

In solving the equations of motion, some approximations, such as neglect of smaller terms, are taken. In order to avoid such approximations, another approach is proposed where the Newton's laws of motion are replaced by the sequences of random numbers. This approach is known as the Monte Carlo simulation.

Though it is easy to manage the numerical experiments as compared to the real experiments, the calculations may not necessarily show the real picture. Depending on the model used, the results may be close to the reality or may be far from the reality. Even if the model used could be the best one, there are still limitations for a numerical simulation:

(i) The number of particles which are some thousands in the model is smaller than the number of particles in a macroscopic object.

(ii) The time required for millions of collisions among the particles is

much smaller than the macroscopic time for the system.

(iii) Since the computer are still not capable to solve many body quantum mechanical wave equations, it is not possible to go for quantum mechanical treatment of a system.

These limitations seem to remain insolvable. However, in the case of weak interaction between particles of a gas, the limitations (i) and (ii) are not too serious.

1. Monte Carlo simulation

Monte-Carlo is a technique used for simulation purposes. The name of this method was chosen Monte-Carlo because of the extensive use of random numbers. At the end of the Second World War to study the diffusion of neutrons in a fissionable material, the Monte Carlo method was developed by von Neumann, Ulam and Metropolis.

Let consider a gas having N particles (molecules) moving in a random manner under the influence of collisions with one another. In the Monte Carlo method, we replace equations of motion by the sequences of random numbers for calculating the trajectories of the particles. In doing so, there are some advantages. First, here we do not use any approximations where small terms are neglected. Secondly, these calculations provide details of motion of each particle at every instant. Such detailed information about trajectories cannot be found in real experiments. Further, the numerical experiments can be easily managed without worrying about the purity of the sample, to maintain low or high temperature as well as density in a gas. Because of these advantages, numerical experiments are getting popularity.

However, we have to find appropriate sequences of random numbers to describe the model. Once the model is set up, the calculations are performed in a well defined manner. Of course, the experimental steps must be correct following the physical scenario. The results however depend on the model employed in the experiment. Validity of the model can however be tested by comparing the results with those of the real experiments.

The design of computer programmes for such experiments depend heavily on the experience of the user. Since the users generally do not published their programs and therefore, one has to develop ones own programme. Besides being useful, these experiments provide deeper understanding of statistical mechanics.

Since the Monte Carlo simulation depends on the sequences of random numbers, we shall now discuss about the random numbers.

2. Random numbers

Random numbers have been in use for scientific purposes for a long time. These numbers have a well defined sequence, but their values change in a random manner. Before the advent of computers, sequences of random numbers were being generated with the help of some events, such as tossing coins, rolling dice, picking up numbers from an urn, etc. These processes for generating random numbers were obviously slow and sometimes unreliable. Moreover, the sequences of random numbers generated by these methods cannot be reproduced. Since random numbers are essentially needed for their application in some techniques, there had been a need to evolve some method for generation of the sequences of random numbers. Since these numbers form a well defined sequence, it may not be appropriate to call them 'random'; a term 'pseudo-random' or 'quasi-random' is often used instead.

From time to time, ideas have been proposed to generate random numbers through some arithmetic manipulations. The advent of computers provided a powerful tool for generating random numbers. Here, we shall discuss about some methods used for the generation of random numbers. Random numbers generated in such methods are reproducible.

2.1 von Neumann approach

von Neumann (1951) suggested the following method to obtain a sequence of random numbers. According to that we start with a four digit number (*e.g.,* 9876), square it (to get 97535376), and extract the middle four digits (5353). Now, we square this number 5353 to get 28654609 and extract the middle four digits to get 6546. This process is repeated to generate a sequence of four digit numbers (9876, 5353, 6546, 8501, 2670, ...). When we get 00 at the end of a number then the number generated further form a loop structure.

Exercise 1. In the von Neumann method, random numbers of four digits are generated in the following manner. We start with a four digit number, square it and extract the middle four digits. This process goes on repeatedly. Start with a four digit number 9876 and generate 20 successive random numbers.

Solution: We start with the four digit number 9876, square of the

number and extract the middle four digits. This extracted number is squared and we again extract the middle four digits. This process goes on and the obtained numbers are given below in the tabular form.

Number	Square	Extract
9876	97535376	5353
5353	28654609	6546
6546	42850116	8501
8501	72267001	2670
2670	7128900	1289
1289	1661521	6615
6615	43758225	7582
7582	57486724	4867
4867	23687689	6876
6876	47279376	2793
2793	7800849	8008
8008	64128064	1280
1280	1638400	6384
6384	40755456	7554
7554	57062916	629
629	395641	3956
3956	15649936	6499
6499	42237001	2370
2370	5616900	6169
6169	38056561	565

The numbers in the first column form a sequence of the required random numbers. These numbers can also be generated by using the following FORTRAN program.

```
c       Random Numbers using von Neumann approach
        open(unit=2, file='random')
        num = 9876

        do 10 i=1, 20
        numsq = num*num
        n3t8 = mod(numsq,1000000)
        n3456 = n3t8/100
        write(2, 20) num, numsq, n3456
        num = n3456
10      continue
```

```
20          format(i6, i12, i6)
            stop
            end
```

2.2 Mixed congruential method

In this method, random numbers are generated with the help of the relation

$$x_{n+1} = (r\ x_n + \mu)(\text{mod}N) \tag{14.1}$$

where mod is the MOD function used in the FORTRAN language, N a positive integer (which is the highest value of the random numbers to be generated), x_n is the n-th random number, r a multiplier, and μ another positive integer (generally taken equal to zero). The $(n+1)$-th random number x_{n+1} is obtained as a remainder when $(rx_n + \mu)$ is divided by N. For the given values of r, N and the starting member x_1, a sequence of numbers, fairly distributed over the range $[0, N]$, is obtained. For the given parameters, after generation of maximum number of random numbers, the numbers start to repeat in the sequence. For example, for $x_1 = 1$, $r = 13$, $N = 100$ and $\mu = 0$, the sequence of random numbers is

1	13	69	97	61	93	9	17	21	73	49	37
81	53	89	57	41	33	29	77				

After that the numbers start to repeat in sequence.

For the generators such as equation (14.1) the important rules are:

(a) Choose a large value of N to maximize the period of the generator.

(b) If N is a power of 2, then choose r so that r mod(8) are 5 or 3.

Exercise 2: Find out random numbers in the mixed congruential method where the first number is 1, multiplier 13 and the number to be added is 2, and the highest value of a random number should not exceed the value 99.

Solution: Here, $x_1 = 1$, $r = 13$, $N = 100$ and $\mu = 2$. Other random numbers can be obtained with the help of the relation

$$x_{n+1} = (rx_n + \mu)(\text{mod}N)$$

The random numbers generated are

1, 15, 97, 63, 21, 75, 77, 3, 41, 35, 57, 43, 61, 95, 37, 83, 81, 55, 17, 23

There are 20 random numbers in the sequence which change in a random manner. The sequence is however periodic in nature. These numbers can also be generated by using the following FORTRAN program.

```
*       Random Numbers using mixed congruential method
        open(unit = 2, file='random')
        integer x1, x2, r, first
        x1 = 1
        first = x1
        r = 13
        n = 100
        mu = 2
10      write(2, *) x1
        x2 = x1 * r + mu
        x1 = mod(x2, n)
        if(x1 .eq. first) stop
        go to 10
        stop
        end
```

2.3 Random numbers uniform on (0, 1)

In the mixed congruential method, the random numbers lie between 0 and $N-1$. When these numbers are divided by N, the random numbers

$$\xi_i = x_i/N$$

would lie between 0 and 1. Thus, ξ_i denotes a random number in the range (0, 1). Since x_i can never exceed $(N-1)$, the sequence repeats and the maximum number of the numbers is $(N-1)$.

Exercise 3. Consider simulation of a neutron moving through a lead wall of thickness $3D$ of an atomic reactor. The neutron is moving in a random manner under collisions with lead atoms. The position of the first collision of the neutron is at a distance D inside the wall, and the mean free-path is D. The neutron is allowed to move randomly for maximum 10 collisions. Use random numbers for expressing directions of motion measured in the clockwise direction relative to the width of the wall. Calculate random numbers in a mixed congruential method where the first number is 1, multiplier 13 and the highest value of a

random number should not exceed the value 99. Consider the motion in the following two situations when the first direction of motion is:

(i) the first random number

(ii) the fifth random number

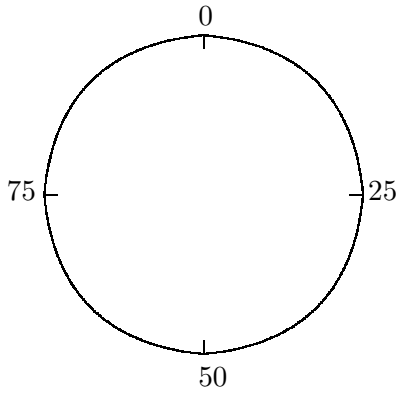
Solution: For $x_1 = 1$, $r = 13$ and $N = 100$, the random numbers generated in the mixed congruential method

$$x_{n+1} = (r\ x_n)(\text{mod}N)$$

are

1	13	69	97	61	93	9	17	21	73	49	37
81	53	89	57	41	33	29	77				

Suppose the random numbers are interpreted as directions in the clockwise direction as shown below.



Each neutron in the reactor wall travels a distance D before colliding with an atom of lead. The neutron then moves in a random direction and travels a distance D again before its next collision, and so on. The thickness of the reactor wall is $3D$. The parallel side of the reactor wall are AB and EF. The first collision is at a distance D inside the wall. That is, the point is at a distance D from the wall side AB

(i) Starting at S with the first random number, 1, the path of the neutron is shown in Fig. a. The neutron obviously gets through the wall after four collisions.

(ii) Starting at S with the fifth random number, 61, the path of the neutron is shown in Fig. b. After ten collisions, the neutron obviously stops inside the wall.

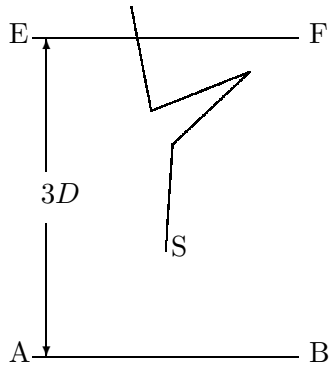


Fig. a

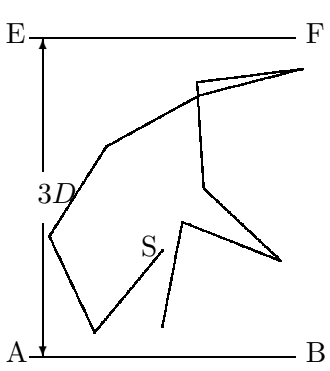


Fig. b

The positions (x, y) can be calculated with the help of a FORTRAN program by using the relations

$$x_{\text{next}} = x_{\text{previous}} + D \sin\Big(\frac{2\pi R}{100}\Big)$$
$$y_{\text{next}} = y_{\text{previous}} + D \cos\Big(\frac{2\pi R}{100}\Big)$$

where R is a random number and the starting point is $(0, D)$. A FORTRAN program written for this is as the following.

```
*       Program for motion of neutron in a reactor
        integer rand1, rand2, r
        open(unit=2, file='simulation')
        rand1 = 61
        r = 13
        n = 100
        mu = 0
        pi = 3.141592654
        depth = 40
        depth3 = 3*depth
        x1 = 0.0
        y1 = depth
        do 10 i=1,10
        angle = 2*pi/100.*rand1
```

```
              x1 = x1 + depth*sin(angle)
              y1 = y1 + depth*cos(angle)
              write(2, 20) rand1, x1, y1
              if(y1 .gt. depth3 .or. y1 .lt. 0.0) stop
              rand2 = rand1*r + mu
              rand1 = mod(rand2, n)
10            continue
20            format(i5, 2f7.2)
              stop
              end
```

The results obtained for the said two cases for $D = 40$ are given in the tabular form below.

Results for the case (i)

Number	x	y
	0.00	40.00
1	2.51	79.92
13	31.67	107.30
69	-5.52	92.58
97	-13.02	131.87

Results for the case (ii)

Number	x	y
	0.00	40.00
61	-25.50	9.18
93	-42.53	45.37
9	-21.10	79.15
17	13.96	98.42
21	52.70	108.36
73	13.02	103.35
49	15.53	63.43
37	44.69	36.05
81	7.50	50.77
53	0.00	11.48

Exercise 4. Consider simulation of a neutron moving through a lead wall of thickness $3D$ of an atomic reactor. The neutron is moving in a random manner under collisions with lead atoms. The position of the first collision of the neutron is at a distance D inside the wall, and the mean free-path is D. The neutron is allowed to move randomly for maximum 10 collisions. Use random numbers for expressing directions of motion measured in the clockwise direction relative to the width of

the wall. Calculate random numbers in a mixed congruential method where the first number is 1, multiplier 19 and the highest value of a random number should not exceed the value 99. Consider the motion in the following two situations when the first direction of motion is:

(i) the second random number

(ii) the first random number

(ii) the fourth random number

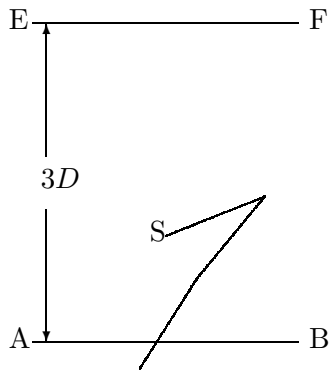
Solution: For $x_1 = 1$, $r = 19$ and $N = 100$, the random numbers generated in the mixed congruential method

$$x_{n+1} = (r\ x_n)(\text{mod}N)$$

are 1, 19, 61, 59, 21, 99, 81, 39, 41, 79.

Suppose the random numbers are interpreted as directions in the clockwise direction as discussed above. Each neutron in the reactor wall travels a distance D before colliding with an atom of lead. The neutron then moves in a random direction and travels a distance D again before its next collision, and so on. The thickness of the reactor wall is $3D$. The parallel side of the reactor wall are AB and EF. The first collision is at a distance D inside the wall. That is, the point is at a distance D from the wall side AB

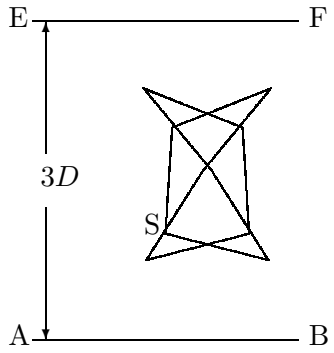
(i) Starting at S with the second random number, 19, the path of the neutron is shown below. The neutron obviously gets through the wall after four collisions.



The positions of the neutron with $D = 40$ are given in the following table.

Number	x	y
	0.00	40.00
19	37.19	54.72
61	11.69	23.90
59	-9.74	-9.87

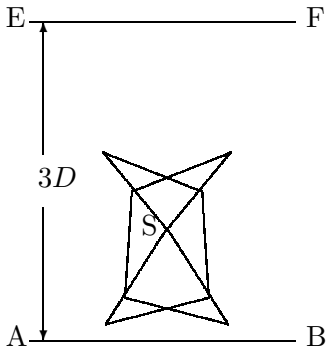
(ii) Starting at S with the first random number, 1, the path of the neutron is shown below. After ten collisions, the neutron obviously moves inside the wall in a closed loop.



The positions of the neutron with $D = 40$ are given in the following table.

Number	x	y
	0.00	40.00
1	2.51	79.92
19	39.70	94.65
61	14.21	63.83
59	-7.23	30.05
21	31.52	40.00
99	29.00	79.92
81	-8.19	94.65
39	17.31	63.83
41	38.74	30.05
79	0.00	40.00

(iii) Starting at S with the fourth random number, 59, the path of the neutron is shown below. After ten collisions, the neutron obviously moves inside the wall in a closed loop. Here the loop is very similar to that in the previous case, but it is shifted in the position.



The positions of the neutron with $D = 40$ are given in the following table.

Number	x	y
	0.00	40.00
59	-21.43	6.23
21	17.31	16.17
99	14.80	56.10
81	-22.39	70.82
39	3.10	40.00
41	24.54	6.23
79	-14.21	16.17
1	-11.69	56.10
19	25.50	70.82
61	0.00	40.00

3. Problems and questions

1. What is difference between the numerical experiment for molecular motion and the Monte Carlo simulation.

2. In the von Neumann method, random numbers of four digits are generated in the following manner. We start with a four digit number, square it and extract the middle four digits. This process goes on repeatedly. Start with a four digit number 7654 and generate 20 successive random numbers.

3. Find out the random numbers in the mixed congruential method where the first number is 1, multiplier 13 and the number to be

added is 2, and the highest value of a random number should not exceed the value 99.

4. Consider simulation of a neutron moving through a lead wall of thickness $3D$ of an atomic reactor. The neutron is moving in a random manner under collisions with lead atoms. The position of the first collision of the neutron is at a distance D inside the wall, and the mean free-path is D. The neutron is allowed to move randomly for maximum 10 collisions. Use random numbers for expressing directions of motion measured in the clockwise direction relative to the width of the wall. Calculate random numbers in a mixed congruential method where the first number is 1, multiplier 13 and the highest value of a random number should not exceed the value 99. Consider the motion in the following two situations when the first direction of motion is:

   (i) the first random number

   (ii) the fifth random number

5. Consider simulation of a neutron moving through a lead wall of thickness $3D$ of an atomic reactor. The neutron is moving in a random manner under collisions with lead atoms. The position of the first collision of the neutron is at a distance D inside the wall, and the mean free-path is D. The neutron is allowed to move randomly for maximum 10 collisions. Use random numbers for expressing directions of motion measured in the clockwise direction relative to the width of the wall. Calculate random numbers in a mixed congruential method where the first number is 1, multiplier 19 and the highest value of a random number should not exceed the value 99. Consider the motion in the following two situations when the first direction of motion is:

   (i) the second random number

   (ii) the first random number

   (ii) the fourth random number

6. Write notes on the following

   (i) Numerical experiments

   (ii) Random numbers

   (iii) Monte Carlo simulation

APPENDICES

A. Relations among thermodynamical quantities

Let us consider a gas specified by its temperature (T), pressure (P), volume (V), entropy (S) and energy (E). Entropy of a body (gas) is a function of its energy

$$S = S(E)$$

Let us consider two bodies having energies E_1 and E_2, and entropies S_1 and S_2, respectively. Suppose, these two bodies form a close system, then the energy E and entropy S of the system are

$$E = E_1 + E_2 \qquad S(E) = S_1(E_1) + S_2(E_2) \tag{A1}$$

Thus, we have

$$\mathrm{d}S = \frac{\mathrm{d}S_1}{\mathrm{d}E_1}\,\mathrm{d}E_1 + \frac{\mathrm{d}S_2}{\mathrm{d}E_2}\,\mathrm{d}E_2 \tag{A2}$$

For a close system, total energy E is conserved, and therefore, from the first part of equation (A1) we have

$$\mathrm{d}E = \mathrm{d}E_1 + \mathrm{d}E_2 = 0 \qquad \text{so that} \qquad \mathrm{d}E_2 = -\mathrm{d}E_1 \tag{A3}$$

Using equation (A3) in (A2), we get

$$\mathrm{d}S = \frac{\mathrm{d}S_1}{\mathrm{d}E_1}\,\mathrm{d}E_1 - \frac{\mathrm{d}S_2}{\mathrm{d}E_2}\,\mathrm{d}E_1 \tag{A4}$$

When the two bodies in the system are in a thermal equilibrium with each other, the entropy S of the system has its maximum value, and thus, for the thermal equilibrium of the two bodies, we have $\mathrm{d}S = 0$ and equation (A4) gives

$$\frac{\mathrm{d}S_1}{\mathrm{d}E_1}\,\mathrm{d}E_1 - \frac{\mathrm{d}S_2}{\mathrm{d}E_2}\,\mathrm{d}E_1 = 0 \qquad \text{or} \qquad \frac{\mathrm{d}S_1}{\mathrm{d}E_1} = \frac{\mathrm{d}S_2}{\mathrm{d}E_2} = \mathrm{C}$$

where C is a constant which should specify the state of the thermal equilibrium between the two bodies. This constant is defined as reciprocal of the absolute temperature T of the bodies in thermal equilibrium. So, we have

$$\frac{1}{T} = \frac{\mathrm{d}S_1}{\mathrm{d}E_1} = \frac{\mathrm{d}S_2}{\mathrm{d}E_2}$$

Since the entropy is a dimensionless quantity, the temperature has dimensions of energy. When the temperature is expressed in Kelvin or degree, T is replaced by kT, where k is a Boltzmann constant ($k = 1.38 \times 10^{-16}$ erg/K). The temperature can also be expressed as

$$T = \left(\frac{\partial E}{\partial S}\right)_V \tag{A5}$$

The pressure P of the gas is expressed as

$$P = -\Big(\frac{\partial E}{\partial V}\Big)_S \tag{A6}$$

The equations (A5) and (A6) can also be jointly written as

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V \tag{A7}$$

Hence,

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}E + \frac{P}{T}\,\mathrm{d}V$$

Therefore,

$$\Big(\frac{\partial S}{\partial V}\Big)_E = \frac{P}{T} \qquad \text{and} \qquad \Big(\frac{\partial S}{\partial E}\Big)_V = \frac{1}{T}$$

(i) Heat function

The heat function H is defined as

$$H = E + PV$$

and thus, we have

$$\mathrm{d}H = \mathrm{d}E + P\mathrm{d}V + V\mathrm{d}P \tag{A8}$$

Using equation (A7) in (A8), we get

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P \tag{A9}$$

Thus, the temperature T and volume V in terms of the heat function W are

$$T = \Big(\frac{\partial H}{\partial S}\Big)_P \qquad \text{and} \qquad V = \Big(\frac{\partial H}{\partial P}\Big)_S$$

(ii) Helmholtz free energy

The Helmholtz free energy F (also known as the free energy) is defined as

$$F = E - TS$$

and thus, we have

$$\mathrm{d}F = \mathrm{d}E - T\mathrm{d}S - S\mathrm{d}T \tag{A10}$$

Using equation (A7) in (A10), we get

$$\mathrm{d}F = -P\mathrm{d}V - S\mathrm{d}T \tag{A11}$$

Thus, the entropy S and pressure P in terms of the Helmholtz free energy F are

$$S = -\Big(\frac{\partial F}{\partial T}\Big)_V \qquad \text{and} \qquad P = -\Big(\frac{\partial F}{\partial V}\Big)_T \tag{A12}$$

Now,

$$E = F + TS \tag{A13}$$

Using equation (A12) in (A13), we get

$$E = F - T\Big(\frac{\partial F}{\partial T}\Big)_V = -T^2\Big(\frac{\partial (F/T)}{\partial T}\Big)_V$$

(iii) Gibbs free energy

The Gibbs free energy G (also known as the thermodynamic potential) is defined as

$$G = E - TS + PV = F + PV = H - TS$$

Thus,

$$\mathrm{d}G = \mathrm{d}E - T\mathrm{d}S - S\mathrm{d}T + P\mathrm{d}V + V\mathrm{d}P \tag{A14}$$

Using equation (A7) in (A14), we get

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P \tag{A15}$$

Thus, the entropy S and volume V in terms of the Gibbs free energy G are

$$S = -\Big(\frac{\partial G}{\partial T}\Big)_P \qquad \text{and} \qquad V = \Big(\frac{\partial G}{\partial P}\Big)_T \tag{A16}$$

Now,

$$H = G + TS \tag{A17}$$

Using equation (A16) in (A17), we get

$$H = G - T\Big(\frac{\partial G}{\partial T}\Big)_P = -T^2\Big(\frac{\partial (G/T)}{\partial T}\Big)_P$$

(iv) Maxwell thermodynamic relations

From the discussion in the previous sections, we have

$$T = \Big(\frac{\partial E}{\partial S}\Big)_V = \Big(\frac{\partial H}{\partial S}\Big)_P \tag{A18}$$

$$P = -\Big(\frac{\partial E}{\partial V}\Big)_S = -\Big(\frac{\partial F}{\partial V}\Big)_T \tag{A19}$$

$$V = \Big(\frac{\partial H}{\partial P}\Big)_S = \Big(\frac{\partial G}{\partial P}\Big)_T \tag{A20}$$

$$S = -\Big(\frac{\partial F}{\partial T}\Big)_V = -\Big(\frac{\partial G}{\partial T}\Big)_P \tag{A21}$$

From equations (A18) and (A19), we have

$$\Big(\frac{\partial T}{\partial V}\Big)_S = \Big(\frac{\partial^2 E}{\partial S \partial V}\Big)_{V,S} \qquad \text{and} \qquad \Big(\frac{\partial P}{\partial S}\Big)_V = -\Big(\frac{\partial^2 E}{\partial S \partial V}\Big)_{V,S}$$

Therefore, we have

$$\Big(\frac{\partial T}{\partial V}\Big)_S = -\Big(\frac{\partial P}{\partial S}\Big)_V \tag{A22}$$

From equations (A18) and (A20), we have

$$\Big(\frac{\partial T}{\partial P}\Big)_S = \Big(\frac{\partial^2 H}{\partial S \partial P}\Big)_{P,S} \qquad \text{and} \qquad \Big(\frac{\partial V}{\partial S}\Big)_P = \Big(\frac{\partial^2 H}{\partial S \partial P}\Big)_{P,S}$$

Therefore, we have

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{A23}$$

From equations (A19) and (A21), we have

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial^2 F}{\partial V \partial T}\right)_{T,V} \qquad \text{and} \qquad \left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial^2 F}{\partial V \partial T}\right)_{T,V}$$

Therefore, we have

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{A24}$$

From equations (A20) and (A21), we have

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial^2 G}{\partial P \partial T}\right)_{T,P} \qquad \text{and} \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial^2 G}{\partial P \partial T}\right)_{T,P}$$

Therefore, we have

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \tag{A25}$$

Equations (A22), (A23), (A24) and (A25) are four Maxwell thermodynamic relations.

(v) Dependence of thermodynamic quantities on the number of particles

So far we have assumed that the number of particles in the given gas is unchanged. When the number of particles in the gas changes, equations (A7), (A9), (A11) and (A15), respectively, modify to the following forms:

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \tag{A26}$$

$$\begin{aligned} \mathrm{d}H &= T\mathrm{d}S + V\mathrm{d}P + \mu\mathrm{d}N \\ \mathrm{d}F &= -P\mathrm{d}V - S\mathrm{d}T + \mu\mathrm{d}N \\ \mathrm{d}G &= -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N \end{aligned} \tag{A27}$$

where μ is the chemical potential and is

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} = \left(\frac{\partial H}{\partial N}\right)_{S,P} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

Equation (A26) can be written as

$$T\mathrm{d}S = \mathrm{d}E + P\mathrm{d}V - \mu\mathrm{d}N$$

and we can have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \qquad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \qquad -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V}$$

For constant pressure and temperature, equation (A27) is

$$\mathrm{d}G = \mu\ \mathrm{d}N$$

Since μ is independent of N, on integration, we get

$$G = \mu N$$

Thus, chemical potential μ of a gas (consisting of identical particles) is the Gibbs free energy per molecule. It obviously depends on the pressure and temperature: $\mu = \mu(P, T)$.

(vi) Grand potential

The grand potential Ω is defined as

$$\Omega = F - \mu N$$

Thus, we have

$$\mathrm{d}\Omega = \mathrm{d}F - \mu\ \mathrm{d}N - N\ \mathrm{d}\mu \qquad (A28)$$

Using equation (A27) in (A28), we get

$$\mathrm{d}\Omega = -S\ \mathrm{d}T - P\ \mathrm{d}V - N\ \mathrm{d}\mu$$

Thus, we have

$$P = -\Big(\frac{\partial\Omega}{\partial V}\Big)_{T,\mu} \qquad S = -\Big(\frac{\partial\Omega}{\partial T}\Big)_{V,\mu} \qquad N = -\Big(\frac{\partial\Omega}{\partial\mu}\Big)_{T,V}$$

(vii) Specific heats

Specific heats of a gas at constant volume (c_V) and constant pressure (c_P) are defined as

$$c_V = \Big(\frac{\partial E}{\partial T}\Big)_V \qquad c_P = \Big(\frac{\partial E}{\partial T}\Big)_P \qquad (A29)$$

Using the relation

$$\mathrm{d}S = \frac{\mathrm{d}E}{T}$$

in equation (A29), we get

$$c_V = T\Big(\frac{\partial S}{\partial T}\Big)_V \qquad c_P = T\Big(\frac{\partial S}{\partial T}\Big)_P$$

Using equation (A12), c_V can also be expressed as

$$c_V = -T\Big(\frac{\partial^2 F}{\partial T^2}\Big)_V$$

(viii) Isothermal compressibility

The isothermal compressibility K_T is defined as

$$K_T = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_T$$

(ix) Adiabatic compressibility

The adiabatic compressibility K_S is defined as

$$K_S = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_S$$

B. Stirling formula

James Stirling derived an important relation according to which, when n is a quite large number, then the logarithm of its factorial is

$$\ln\, n! = n\, \ln\, n - n$$

Proof of this relation can be given in the following manner.

$$\ln\, n! = \ln\, (1.2.3. \ldots n) = \sum_{p=1}^{n} \ln\, p \qquad (B1)$$

As compared to the variation of a large number, its logarithm varies very slowly. Therefore, the sum in equation (B1) can be replaced by an integration, and thus we have

$$\ln\, n! \approx \int_1^n \ln\, p\, \mathrm{d}p = \Big[p\, \ln\, p - p\Big]_1^n = n\, \ln\, n - n + 1$$

Since n is quite large, we have

$$\ln\, n! = n\, \ln\, n - n$$

It can also be written as

$$\ln\, n! = n\, \Big[\ln\, n - 1\Big] = n\, \ln(n/e) = \ln(n/e)^n$$

Thus, on taking antilogarithm, we have

$$n! = (n/e)^n$$

C. Number of quantum states

Here, we shall expressions for the number of quantum states (i) in the energy range from E to $E + \mathrm{d}E$, (ii) in the momentum range from p to $p + \mathrm{d}p$, and (iii) in the frequency range from ν to $\nu + \mathrm{d}\nu$.

(i) in the energy range from E to $E + \mathrm{d}E$

Let consider non-interacting or weakly interacting particles having energy in the range from E to $E + \mathrm{d}E$ enclosed in a volume V in three dimensional space. In the phase space, volume of a unit cell is h^3, and a finite volume available to each particle is

$$\int \mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z\ \mathrm{d}p_x\ \mathrm{d}p_y\ \mathrm{d}p_z$$

Hence, the number g of unit cells in the volume of phase space is

$$g = \frac{1}{h^3} \int \mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z\ \mathrm{d}p_x\ \mathrm{d}p_y\ \mathrm{d}p_z \qquad (C1)$$

The integral over the space coordinates gives the physical volume V available to the particles

$$\int \mathrm{d}x\ \mathrm{d}y\ \mathrm{d}z = V$$

The integral over the momentum coordinates can be calculated in the following manner. For a particle of mass m and energy E, the momentum components p_x, p_y, p_z have the relation

$$p_x^2 + p_y^2 + p_z^2 = 2mE$$

Hence, for a particle of energy E, in the momentum space (with coordinates p_x, p_y, p_z), we shall have a sphere of radius $\sqrt{2m\ E}$. In order to include particles having energies from E to $E + \mathrm{d}E$, we have concentric spheres having radii in the range from $\sqrt{2m\ E}$ to $\sqrt{2m(E + \mathrm{d}E)}$. Hence, for the particles having energies from E to $E + \mathrm{d}E$, we have

$$\int \mathrm{d}p_x\ \mathrm{d}p_y\ \mathrm{d}p_z = \frac{4\pi}{3}\Big\{\sqrt{2m(E + \mathrm{d}E)}\Big\}^3 - \frac{4\pi}{3}\Big\{\sqrt{2mE}\Big\}^3$$

$$= \frac{4\pi}{3}\big(2mE\big)^{3/2}\Big[\Big(1 + \frac{\mathrm{d}E}{E}\Big)^{3/2} - 1\Big]$$

$$= \frac{4\pi}{3}\big(2mE\big)^{3/2}\Big[1 + \frac{3}{2}\ \frac{\mathrm{d}E}{E} + \ldots - 1\Big]$$

$$= \frac{4\pi}{3}\big(2mE\big)^{3/2}\ \frac{3}{2}\frac{\mathrm{d}E}{E} = 2\pi E^{1/2}\big(2m\big)^{3/2}\mathrm{d}E$$

Thus, the number of cells $g(E)\mathrm{d}E$ in the energy range from E to $E + \mathrm{d}E$ is (using equation C1)

$$g(E)\ \mathrm{d}E = \frac{1}{h^3}\ V 2\pi E^{1/2}(2m)^{3/2}\ \mathrm{d}E = 2\pi V\Big(\frac{2m}{h^2}\Big)^{3/2}\ E^{1/2}\ \mathrm{d}E$$

For the particles, such as electrons, each having two possible values of spin quantum number, $1/2$ and $-1/2$, the number of quantum states is two times that given above. Thus, we have

$$g(E)\ \mathrm{d}E = 4\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\ \mathrm{d}E$$

or in general, we have

$$g(E)\ \mathrm{d}E = 2\pi g V\Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\ \mathrm{d}E$$

where g is the degeneracy of the state.

(ii) in the momentum range from p to $p + \mathrm{d}p$

For finding out the number of cells in the momentum range from p to $p + \mathrm{d}p$, we use the relation for non-interacting or weakly interacting particles (potential energy is zero)

$$E = \frac{p^2}{2m} \qquad \text{and} \qquad \mathrm{d}E = \frac{p}{m}\ \mathrm{d}p \qquad (C2)$$

Thus, the number of cells in the momentum range from p to $p + \mathrm{d}p$ is

$$g(p)\ \mathrm{d}p = g(E)\ \mathrm{d}E = 2\pi V\Big(\frac{2m}{h^2}\Big)^{3/2} E^{1/2}\ \mathrm{d}E$$

$$= 2\pi V\Big(\frac{2m}{h^2}\Big)^{3/2}\ \frac{p}{\sqrt{2m}}\frac{p}{m}\ \mathrm{d}p = \frac{4\pi V p^2}{h^3}\ \mathrm{d}p$$

where equation (C2) is used.

(iii) in the frequency range from ν to $\nu + \mathrm{d}\nu$

The number of cells in the momentum range from p to $p + \mathrm{d}p$ is

$$g(p)\ \mathrm{d}p = \frac{4\pi V p^2}{h^3}\ \mathrm{d}p$$

For a photon of frequency ν, we have momentum

$$p = \frac{h\nu}{c} \qquad \text{so that} \qquad \mathrm{d}p = \frac{h}{c}\ \mathrm{d}\nu$$

Now, the number of quantum states lying in the frequency range from ν to $\nu + \mathrm{d}\nu$ is

$$g(\nu)\ \mathrm{d}\nu = g(p)\mathrm{d}p = \frac{4\pi V}{h^3}\ \left(\frac{h\nu}{c}\right)^2 \frac{h}{c}\ \mathrm{d}\nu = \frac{4\pi V\nu^2}{c^3}\ \mathrm{d}\nu$$

Photons of the same energy can have two different directions of polarization: circularly clockwise and circularly anti-clockwise. Taking this aspect into account, we have

$$g(\nu)\ \mathrm{d}\nu = 2\ \frac{4\pi V\nu^2}{c^3}\ \mathrm{d}\nu = \frac{8\pi V\nu^2}{c^3}\ \mathrm{d}\nu$$

D. Hypergeometric functions

$$\sinh x = \frac{\mathrm{e}^x - \mathrm{e}^{-x}}{2} \qquad \cosh x = \frac{\mathrm{e}^x + \mathrm{e}^{-x}}{2} \qquad \tanh x = \frac{\mathrm{e}^x - \mathrm{e}^{-x}}{\mathrm{e}^x + \mathrm{e}^{-x}}$$

$$\mathrm{cosech}\ x = \frac{1}{\sinh x} \qquad \mathrm{sech}\ x = \frac{1}{\cosh x} \qquad \coth x = \frac{1}{\tanh x}$$

$$\cosh^2 x = \sinh^2 x + 1; \qquad \coth^2 x = 1 + \mathrm{cosech}^2 x; \qquad \tanh^2 x + \mathrm{sech}^2 x = 1$$

$$\sinh\,(2x) = 2\,\sinh x\,\cosh x; \qquad \cosh\,(2x) = 2\,\cosh^2 x - 1 = 1 + 2\,\sinh^2 x$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\big(\sinh x\big) = \cosh x; \qquad \frac{\mathrm{d}}{\mathrm{d}x}\big(\cosh x\big) = \sinh x; \qquad \frac{\mathrm{d}}{\mathrm{d}x}\big(\tanh x\big) = \mathrm{sech}^2 x$$

E. Gamma function

The gamma function, denoted by $\Gamma(z)$, is defined as

$$\Gamma(z) = \int_0^\infty \mathrm{e}^{-t}\ t^{z-1}\mathrm{d}t \qquad \text{for} \quad z > 0 \qquad (E1)$$

where z is treated as a constant during integration.

(i) We have

$$\Gamma(1) = \int_0^\infty \mathrm{e}^{-t}\mathrm{d}t = \Big[-\mathrm{e}^{-t}\Big]_0^\infty = 1$$

(ii) Recurrence relation can be derived as

$$\Gamma(z+1) = \int_0^\infty \mathrm{e}^{-t}\ t^z\ \mathrm{d}t$$

On integrating by parts, we get

$$\Gamma(z+1) = \left[t^z(-\mathrm{e}^{-t})\right]_0^\infty - \int_0^\infty z\ t^{z-1}(-\mathrm{e}^{-t})\mathrm{d}t$$

$$= 0 + z\int_0^\infty \mathrm{e}^{-t}\ t^{z-1}\ \mathrm{d}t = z\ \Gamma(z)$$

Hence, the recurrence relation is

$$\Gamma(z+1) = z\ \Gamma(z)$$

(iii) Thus, when n is an positive integer, we have

$$\Gamma(n+1) = n\ \Gamma(n) = n(n-1)\ \Gamma(n-1) = \cdots = n(n-1)(n-2)\cdots 2\ \ 1 = n!$$

Hence,

$$\Gamma(n+1) = n!$$

(iv) Putting

$$t = x^2 \qquad \text{so that} \qquad \mathrm{d}t = 2x\ \mathrm{d}x$$

in equation (E1), we get

$$\Gamma(z) = 2\int_0^\infty \mathrm{e}^{-x^2} x^{2z-1}\ \mathrm{d}x$$

This is another expression for the gamma function.

(v) We have

$$\Gamma(1/2) = 2\int_0^\infty \mathrm{e}^{-x^2}\ \mathrm{d}x \qquad (E2)$$

Similarly, we can write

$$\Gamma(1/2) = 2\int_0^\infty \mathrm{e}^{-y^2}\ \mathrm{d}y \qquad (E3)$$

Multiplication of equations (E2) and (E3), we get

$$[\Gamma(1/2)]^2 = 4\int_0^\infty \mathrm{e}^{-x^2}\ \mathrm{d}x \int_0^\infty \mathrm{e}^{-y^2}\ \mathrm{d}y = 4\int_{x=0}^\infty \int_{y=0}^\infty \mathrm{e}^{-(x^2+y^2)}\ \mathrm{d}x\ \mathrm{d}y$$

If we use, $\quad x = r\cos\theta \quad$ and $\quad y = r\sin\theta$

we have $\quad \mathrm{d}x\ \mathrm{d}y = r\ \mathrm{d}r\ \mathrm{d}\theta \quad$ and $\quad x^2 + y^2 = r^2$

Further, the limits for x, from 0 to ∞ and for y, from 0 to ∞ cover the first quadrant of a graph-paper. The same region can be covered through the limits for r, from 0 to ∞ and for θ, from 0 to $\pi/2$. Thus, we have

$$[\Gamma(1/2)]^2 = 4 \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \mathrm{e}^{-r^2} r \, \mathrm{d}r \, \mathrm{d}\theta$$

$$= 4 \, \frac{\pi}{2} \int_{r=0}^{\infty} \mathrm{e}^{-r^2} r \, \mathrm{d}r = 2\pi \Big[- \frac{\mathrm{e}^{-r^2}}{2} \Big]_0^{\infty} = \pi$$

Thus,

$$\Gamma(1/2) = \sqrt{\pi}$$

(vi) We can use the relation, $\Gamma(x) = \Gamma(x+1)/x$ to calculate $\Gamma(x)$ for negative values of x. For example,

$$\Gamma(-1/2) = \frac{\Gamma(1/2)}{-1/2} = -2 \, \sqrt{\pi}$$

(vii) The function $\Gamma(x)$ at $x = 0$ is however singular.

Consequently, for the negative integer values of x, $\Gamma(x)$ is singular. Therefore, for a non-singular value of $\Gamma(x)$, x must be a positive integer.

F. Useful integrals

(i) We have

$$I = \int_0^{\infty} x^n \, \mathrm{e}^{-ax^2} \, \mathrm{d}x$$

Let $x = y^{1/2}/a^{1/2}$, and therefore, $\mathrm{d}x = (y^{-1/2}/2a^{1/2}) \, \mathrm{d}y$. Then, we have

$$I = \frac{1}{2 \, a^{(n+1)/2}} \int_0^{\infty} y^{(n-1)/2} \, \mathrm{e}^{-y} \, \mathrm{d}y = \frac{1}{2 \, a^{(n+1)/2}} \, \Gamma[(n+1)/2]$$

Thus,

$$\int_0^{\infty} \mathrm{e}^{-ax^2} \, \mathrm{d}x = \frac{1}{2} \, \sqrt{\frac{\pi}{a}} \qquad \int_0^{\infty} x \, \mathrm{e}^{-ax^2} \, \mathrm{d}x = \frac{1}{2a}$$

$$\int_0^{\infty} x^2 \, \mathrm{e}^{-ax^2} \, \mathrm{d}x = \frac{1}{4a} \, \sqrt{\frac{\pi}{a}} \qquad \int_0^{\infty} x^3 \, \mathrm{e}^{-ax^2} \, \mathrm{d}x = \frac{1}{2a^2}$$

$$\int_0^{\infty} x^4 \, \mathrm{e}^{-ax^2} \, \mathrm{d}x = \frac{3}{8a^2} \, \sqrt{\frac{\pi}{a}} \qquad \int_0^{\infty} x^5 \, \mathrm{e}^{-ax^2} \, \mathrm{d}x = \frac{1}{a^3}$$

(ii) We have

$$I = \int_0^\infty x^n \, \mathrm{e}^{-ax} \, \mathrm{d}x$$

Let $x = y/a$, and therefore, $\mathrm{d}x = \mathrm{d}y/a$. Then, we have

$$I = \frac{1}{a^{n+1}} \int_0^\infty y^n \, \mathrm{e}^{-y} \, \mathrm{d}y = \frac{1}{a^{n+1}} \, \Gamma(n+1)$$

Thus,

$$\int_0^\infty x^{1/2} \, \mathrm{e}^{-ax} \, \mathrm{d}x = \frac{\sqrt{\pi}}{2 \, a^{3/2}} \qquad \int_0^\infty x \, \mathrm{e}^{-ax} \, \mathrm{d}x = \frac{1}{a^2}$$

$$\int_0^\infty x^{3/2} \, \mathrm{e}^{-ax} \, \mathrm{d}x = \frac{3\sqrt{\pi}}{4 \, a^{5/2}} \qquad \int_0^\infty x^2 \, \mathrm{e}^{-ax} \, \mathrm{d}x = \frac{2}{a^3}$$

$$\int_0^\infty x^{5/2} \, \mathrm{e}^{-ax} \, \mathrm{d}x = \frac{15\sqrt{\pi}}{8 \, a^{7/2}} \qquad \int_0^\infty x^3 \, \mathrm{e}^{-ax} \, \mathrm{d}x = \frac{6}{a^4}$$

G. Time-dependent correlation function

Dynamical properties of a fluid can be explained in terms of time-dependent correlation functions. The time-dependent correlation function of two dynamical variables, $A(t) \equiv A[\vec{r}\,(t), \vec{p}\,(t)]$ and $B(t) \equiv B[\vec{r}\,(t), \to p(t)]$, is defined as an ensemble average

$$C_{AB}(\tau) = \big\langle A(t+\tau) \; B(t) \big\rangle$$

We are aware of the fact that an ensemble average can be taken equivalent to a time average, so that

$$\big\langle A(t+\tau) \; B(t) \big\rangle = \overline{A(t+\tau) \; B(t)} \equiv \lim_{T \to \infty} \int_{t'=0}^{T} A(t+\tau+t') \; B(t+t') \; \mathrm{d}t'$$

For $A = B$, the time-dependent correlation function is

$$C_A(\tau) = \big\langle A(t+\tau) \; A(t) \big\rangle$$

Thus, we have

$$C_A(0) = \big\langle A^2(t) \big\rangle \equiv \big\langle A^2(t+\tau) \big\rangle$$

It is also known as the time auto-correlation function of A.

For an isolated system, the correlation function is independent of time and therefore, it is stationary. Thus, the correlation functions of two variables A and B of an isolated system is (putting $t = 0$)

$$C_{AB}(\tau) = \big\langle A(\tau) \; B(0) \big\rangle \qquad (G1)$$

and it satisfies the condition

$$\frac{\mathrm{d}}{\mathrm{d}t}C_{AB}(\tau) = 0 \qquad (G2)$$

Using equation (G1) in (G2), we get

$$\frac{\mathrm{d}}{\mathrm{d}t}\big\langle A(\tau)\ B(0)\big\rangle = 0$$

$$\big\langle\ \dot{A}\ (\tau)\ B(0)\big\rangle + \big\langle A(\tau)\ \ \dot{B}\ (0)\big\rangle = 0$$

$$\big\langle\ \dot{A}\ (\tau)\ B(0)\big\rangle = -\big\langle A(\tau)\ \ \dot{B}\ (0)\big\rangle$$

For $A = B$, we have

$$\big\langle\ \dot{A}\ (\tau)\ A(0)\big\rangle = 0$$

The time-correlation of fluctuation in a variable A, expressed by

$$\delta A(\tau) = A(t) - \big\langle A\big\rangle \qquad \text{is} \qquad C_A(\tau) = \big\langle \delta A(t+\tau)\ \delta A(t)\big\rangle$$

Fourier transform of $A(t)$ is

$$A(\omega) = \int_{-\infty}^{\infty} A(t)\ \exp(i\omega t)\ \mathrm{d}t$$

and the inverse Fourier transform is

$$A(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} A(\omega)\ \exp(-i\omega t)\ \mathrm{d}\omega$$

Some specific properties of the fluctuation function

(i) When τ is very large, the $A(t)$ and $A(t+\tau)$ become uncorrelated, *i.e.,* if $\big\langle A\big\rangle = 0$, we have

$$\lim_{\tau\to\infty} C_A(\tau) = \lim_{\tau\to\infty} \big\langle A(t+\tau)\ A(t)\big\rangle = 0$$

(ii) For any value of τ, the magnitude of $C_A(\tau)$ cannot exceed the value of $C_A(0)$. That is

$$C_A(\tau) \le C_A(0)$$

This inequality can be proved by expanding the relation

$$\big\langle |A(t) \pm A(t+\tau)|^2\big\rangle = \big\langle A^2(t)\big\rangle + \big\langle A^2(t+\tau)\big\rangle \pm 2\ \big\langle A(t)\ A(t+\tau)\big\rangle$$

$$= C_A(0) + C_A(0) \pm 2\ C_A(\tau) = 2\ [C_A(0) \pm C_A(\tau)] \ge 0$$

Thus, we must have

$$|C_A(\tau) \le C_A(0)| \qquad \text{for all} \quad \tau$$

(iii) The function $C_A(\tau)$ is symmetric about $\tau = 0$, *i.e.*,

$$C_A(\tau) = C_A(-\tau)$$

This relation can be proved by substituting t for $t - \tau$

$$C_A(\tau) = \big\langle A(t)\ A(t+\tau)\big\rangle = \big\langle A(t-\tau)\ A(t)\big\rangle = \big\langle A(t)\ A(t-\tau)\big\rangle = C_A(-\tau)$$

Physical constants

Physical constant	Value
Avogadro number A	6.02×10^{23} mol^{-1}
Boltzmann constant k	1.38×10^{-23} Joule/K
Planck constant h	6.63×10^{-34} Joule-sec
Electron mass m	9.11×10^{-31} kg
Electron charge e	1.60×10^{-19} Coulomb
Proton mass m_p	1.67×10^{-27} kg
Speed of light c	3.00×10^{8} m s^{-1}
Gas constant R	8.31 J mol^{-1} K^{-1}

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